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on Carbon Dioxide Utilization***



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**Preprinted Abstracts
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Oral Presentation

Halogen-Free Process for the Conversion of Carbon Dioxide to Urethanes by Heterogeneous Catalysis

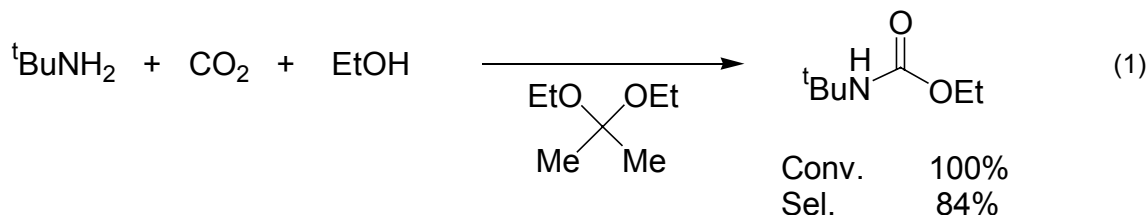
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National Institute of Advanced Industrial Science and Technology

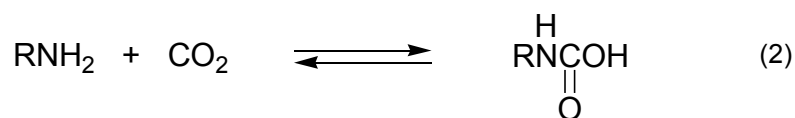
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The development of environmentally friendly industrial process using carbon dioxide as a cheap and safe C1 building block has attracted much interest. Especially, possibility as a phosgene alternative is quite attractive. We report here the urethane synthesis *via* the reaction of dense carbon dioxide catalyzed by tin compounds (eq 1). Dibutyltin oxide is an active catalyst for the present urethane synthesis. Other tin compounds such as $\text{Bu}_2\text{Sn}(\text{OMe})_2$ and Me_2SnCl_2 also exhibit the catalytic activities while no reaction take place in the absence of the catalysts. In order to achieve high yields, the addition of acetals is quite effective. This is presumably due to the role of acetals as a dehydrating agent.



The major side reactions in eq 1 are i) imine formation and ii) amine alkylation by alcohols. A high CO_2 pressure shifts eq 2 toward the carbamic acid. This will prevent the side reactions resulting in improvement of the selectivity. The scope and limitations of this new process will be discussed.



Acknowledgment. This study was supported by Industrial Technology Research Grant Program in 2000 from the New Energy and Industrial Technology Development Organization (NEDO) of Japan.

Poster Presentation

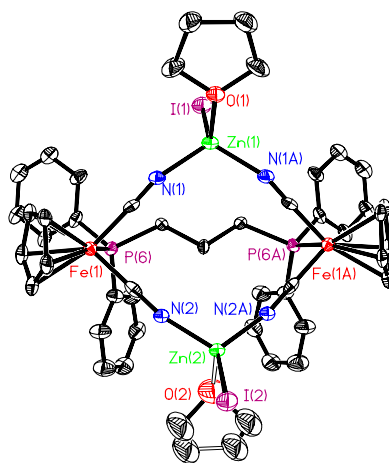
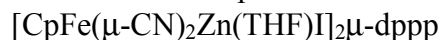
The Use of Double Metal Cyanides for the Coupling of Epoxides and CO₂

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The coupling of CO₂ and epoxides to form polycarbonates is of much interest due to its use as an inexpensive and environmentally friendly monomer as well as the interesting physical properties of the copolymer.¹ Metal based catalysts for this copolymerization are hindered by the ability of these polymers to degrade to form cyclic carbonate species.² Patents by Dow and ARCO have shown Double Metal Cyanides (DMC) to be useful for the formation polycarbonate, since little cyclic carbonate formation is seen. These DMC catalysts are made from the aqueous reaction of K₃Fe(CN)₆ with ZnCl₂ followed by homogenization with a diglycol support to form the active catalyst species. Although effective at copolymerization, little is known about the nature of these heterogeneous catalysts.³

In order to study DMC as copolymerization catalysts, we've designed and characterized soluble model catalysts using KCpFe(CN)₂(L) as a metallocyanide source (where L = CO, PR₃, or PR₂(CH₂)_nPR₂). The reaction of these metallocyanides with ZnI₂ form soluble, diamond shaped DMC species as seen in the crystal structure of [CpFe(μ-CN)₂Zn(THF)I]₂μ-dppp below. Organometallic DMC catalysts should prove highly tunable by changing functional groups on the Cp ring as well as at the (L) position. Synthesis and reactivities of these species will be discussed.



References:

- 1) Kendall, J. L.; Canelas, D. A.; Young, J. L.; DeSimone, J. M. *Chem. Rev.* **1999**, 99, 543.
- 2) Rokicki, A.; Kuran, W. *J. Macromol. Sci. Rev. Macromol. Chem.* **1981**, C21, 135.
- 3) U. S. Patent 4,500,704 1985 to Kruper, Dow Chemical Company

Poster Presentation
Economic advantages of technology of burning fuel
with way production and effective utilization CO₂

The member of International Power Academy, doctor of engineering science, professor R. Akhmedov, doctor of economic sciences E. Akhmedov (joint-stock company "ECOEN"), The diploma – engineer B. Barochin (State Power institute "Vnpienergoprom"), Russia.

At traditional methods of burning of various kinds of organic fuel in combustion gases the volumetric ratio CO₂ is insignificant and usually does not exceed 10-12 %. The flue gases with the so low contents CO₂ are not introduce values for beneficial use, and the extraction of carbon dioxide from products of burning with the help of known technologies manages rather dearly.

So, for example, at use of most effective absorption ways on the basis of applying Monoethanolamin (MEA) the energy output of production reaches 35.2 mJ / kg CO₂. Cost of a commercial production CO₂ in the advanced countries on the data of the Montreal Protocol 1995 reaches 1.9 \$ / kg.

High cost of production CO₂ sharply limits its applying as valuable raw material or reactant in numerous productions. As a rule, it is applied only as inexpensive waste of some chemical productions.

Last years in Russia (joint-stock company "ECOEN") the ecologically safe technology of burning of any kinds of fuel was designed and tested, at which one receive combustion gases with high concentration CO₂, reaching 99 - 100 %, that excludes necessity of application of any other expensive methods of production CO₂.

The opportunity of application of the considered technology in typical heat power installations was in details investigated is experimentally proved. Heat power installations working at such an ecologically secure mode was called EcoTES.

The cheap carbonic acid can find wide application in various technologies. Among of set of technologies, in which it is possible rationally to utilize cheap carbon dioxide, one of most large-scale, effective and prepared for practical realization is the application EcoTES on petroleum fields. Thus, as shows long and successful experience of USA, is reached significant not only ecological, but also economic benefit at the expense of a burial of greenhouse gases, production of additional energy on the basis of rational use of way gases, burnt in open torches, and also - essential enhance of oil recovery (EOR) at the expense of repressuring CO₂ in petroleum layers.

The results of the executed researches are protected by the patents, have passed expertise in a number of leading scientific and design institutes, and also were approved and recommended to practical realization by Scientific and Technical council of the Ministry of power of Russian Federation.

The design development of head demonstration and pilot plants by productivity from 1600 up to 36000 t CO₂ / a year, and also feasibility reports of industrial plants by capacity up to 300 mWt with production over one million t CO₂ per one year are now executed.

Thus, the energy output of production CO₂ does not exceed 2.9 - 4.1 mJ/ kg CO₂, or 0.07 - 0.1 kW·H / kg CO₂ and its cost price - is not higher, than 0.6 - 1.0 cents of USA on kg CO₂.

Poster Presentation

Electrochemical reduction of CO₂ in high pressure CO₂-Methanol systems

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The electrochemical reduction of CO₂ is investigated mainly in the aqueous solutions and under ambient conditions, since water is used as a reduction agent. In that case, the partial current of CO₂ reduction is limited by mass transport of CO₂ because of its low solubility in water. From the viewpoint of high mass transport, use of liquid CO₂ electrolyte is noteworthy, but enough conductivity cannot be obtained in this case because CO₂ is non-polar. As an alternative, we have previously reported the use of CO₂-methanol solution under high pressures to achieve high CO₂ concentration and thus high mass transport. In this report, we present the effect of supporting salts and the useful utilization of CO for fuel synthesis.

In order to use water as an electron donor, we have performed electrolysis in a two-compartment cell. In this cell, the cathode compartment was filled with CO₂-methanol solution, while the other compartment containing aqueous electrolyte with ammonium perchlorate as supporting salt. At the Ag cathode, electrolysis was conducted in CO₂-methanol medium containing various supporting salts (NH₄BF₄, TBABF₄, NH₄ClO₄, TBAClO₄, and LiClO₄) under CO₂ atmosphere at 40-atm pressure. An electrical charge of 6.8 C was passed galvanostatically at 200 mA/cm². In case of TBABF₄ and LiClO₄, the major products were H₂ and CO with a distribution ratio CO : H₂ = 1 : 1. On the other hand, in case of NH₄BF₄, NH₄ClO₄, and TBAClO₄, major reduction product was H₂.

Dimethyl ether (DME) is emerging as a non-polluting fuel for a wide array of applications, such as transportation fuel, household fuel and fuel for electric power generation. CO and H₂, which are source gases for DME synthesis, are produced in a ratio of 1:1 by electrochemical reduction of CO₂. Therefore, in view of reducing CO₂ emission to prevent global warming and developing technology for the production of DME raw materials, the present electrochemical CO₂ reduction method is a promising one for practical fixation process.

Acknowledgments

The present work was mainly supported by New Energy and Industrial Technology Development Organization (NEDO).

Poster Presentation

Reaction of ketals with carbon dioxide in organic solvents and in SC-CO₂

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The synthesis of carbonates from alcohols (Eq. 1) is a good example of "green chemistry" that implements the atom economy principle. Nevertheless, its exploitation is limited by kinetic and thermodynamic factors. Among others, the formation of water that remains in the reaction medium may have a negative influence on the carbonate yield.

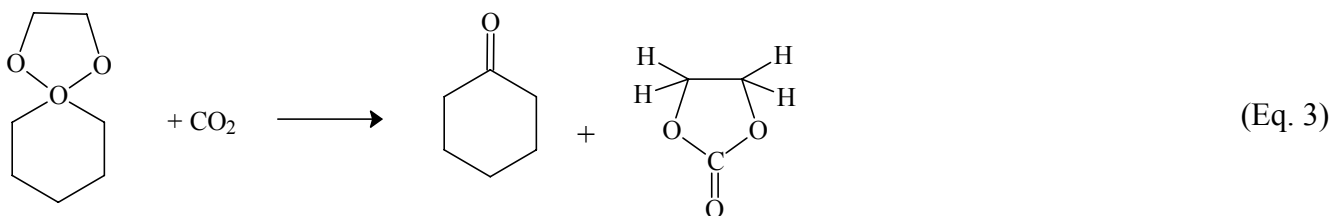


A strategy for circumventing such negative influence, is to carry out the reaction in two steps, or by using a special technology, that avoids the presence of water in the environment where the carbonate is formed. A possible implementation of such strategy is to react alcohols with ketons to form a ketal.



The subsequent reaction of ketals with carbon dioxide (Eq. 3) may bring to the synthesis of cyclic or linear carbonates, avoiding the presence of water in the reaction medium.

We have tested reaction 3 in both conventional organic solvents under 60 atm CO₂ and in SC-CO₂ at various pressures and temperatures, using several catalysts.



Interestingly, with the same catalyst, the use of SC-CO₂ allows the formation of the carbonate that is not observed in conventional organic solvents and 60 atm-CO₂.

Oral Presentation

Carbon Dioxide Utilization in Developing Innovative Synthetic Methodologies

Michele Aresta*, Angela Dibenedetto

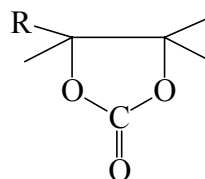
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The chemical industry can contribute to reducing the carbon dioxide emission by direct and indirect routes. Innovative technologies which implement the principles of atom-economy, dematerialization, energy saving, and raw material diversification are example of the latter.

The utilization of carbon dioxide in the synthesis of chemicals is a direct route to CO₂ recycling.

In this paper selected types of molecular compounds prepared from CO₂ (such as organic monomeric (linear, **1** or cyclic, **2**) carbonates,



carbamates, isocyanates, carboxylic acids) are considered and the life cycle assessment methodology is applied in order to ascertain the main advantages of the use of CO₂. In addition, the synthesis of methanol from CO₂ or CO is assessed using LCA, evaluating the environmental-economic-energetic benefits of the use of CO₂.

Oral Presentation
**Enantioselective Nb-catalyzed synthesis of organic cyclic carbonates
based on carbon dioxide utilisation**

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In this paper we discuss the synthesis of cyclic carbonates from either CO₂/O₂ and olefins, or from optically active or racemic epoxides and CO₂ catalyzed by niobium compounds.

Synthetic methodologies based on carbon dioxide utilization have received attention and few examples can be found in the literature of use of homogeneous and heterogeneous catalysts in the carboxylation of epoxides.

The oxidative carboxylation of olefins has a great potential. It uses cheap materials as olefins, carbon dioxide and oxygen, to afford valuable chemicals and couples two processes: the epoxidation of the olefin and the carboxylation of the epoxides. It can be considered an innovative methodology as very few data are present in the literature.

We have focused our attention on Nb₂O₅, Nb(IV) and Nb(V) compounds as catalysts in the fixation of carbon dioxide in several epoxides (cyclic and linear) and in the direct oxidative carboxylation of olefins.

By using niobium compounds the stereochemistry of the insertion of CO₂ into epoxides is strictly controlled. In fact, starting from pure enantiomers the relevant pure carbonates can be isolated in very high yield and selectivity (ee>99%) and no formation of byproducts is observed. The use of homogeneous catalysts with optically active ligands also affords interesting results. They have quite interesting catalytic activity and give interesting ee. These catalysts have been used in the synthesis of optically active carbonates starting from racemic mixtures of epoxides.

We have also studied the activity of Nb₂O₅ or of Nb(IV) and Nb(V) homogeneous complexes in the direct oxidative carboxylation of olefins and found that the reaction path is strongly influenced by the experimental conditions. By controlling temperature, pressure of oxygen, solvent and by using a mixture of Nb₂O₅ and NbCl₅ the carbonate yield is quite interesting and approaches 28-30%.

Studies are now in progress in order to find optically active catalysts, which may promote the direct oxidative carboxylation of olefins to afford pure enantiomeric carbonates.

Poster Presentation
**THE PARAMETERS OF METHANE KINETIC BURNING
IN THE OXIDATION MEDIUM ($O_2 + CO_2$)**

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For poster presentation

For effective evolving of carbon dioxide from combustion products it is suggested that the industrial burning up of organic fuels should be held not in air but in the oxidation medium ($O_2 + CO_2$) [1]. Besides while hydrocarbons burn in air nitrogen oxides are formed in combustion products, which is impossible if we substitute nitrogen for CO_2 in the oxidation medium. In the first case the concentration of carbon dioxide in the products of combustion may reach 98 - 99 % after water vapour condensation. Carbon dioxide which is formed is not thrown into the atmosphere but is used for various purposes, e.g. for the needs of food industry or fire-fighting.

The experiments showed that if we want to have the ($O_2 + CO_2$) mixture instead of air as an oxidizer we can't do it just by simple substitution of 79 % of N_2 for the same amount of CO_2 . Because of the essential difference in thermophysical properties of nitrogen and carbon dioxide such parameters of combustion as normal velocity of flame propagation and the temperature of combustion will greatly change.

When oxygen concentration in the oxidation medium ($O_2 + CO_2$) is 21 % (like in air) burning of methane is impossible. To keep the main parameters of furnace operation the same the composition of oxidation medium ($O_2 + CO_2$) needs to be optimized. To reach the combustion temperature which is typical of stoichiometric air-methane mixtures oxygen concentration in the oxidation medium ($O_2 + CO_2$) should be increased up to 34 %. To achieve the same velocity of flame propagation it should be as high as 38 %.

The examination of kinetic flame stability in the burner showed that in the process of methane burning in the oxidation medium ($0.36O_2 + 0.64CO_2$), breaking through and separation of flame take place at considerably greater velocities of gas mixture current. In general the region of stable methane burning in such a medium is wider than in air. The application of stabilizers makes it possible to increase the maximum velocity of flame separation more.

The analysis of thermodynamic balance in the combustion zone when ($CH_4 + O_2 + CO_2$) mixtures are burnt shows that the substitution of ballast nitrogen for CO_2 leads to the equilibrium $2CO + O_2 \rightleftharpoons 2CO_2$ shifting to the formation of CO. However the relative amount of CO/ CO_2 decreases. When stoichiometric mixtures of methane and oxidation medium ($0.36 O_2 + 0.64 CO_2$) with a slight excess of the latter burn nearly all CO changes into CO_2 by the moment of combustion products temperature reduction up to 1000 - 1200 K. In the cooled products of combustion it doesn't exist.

1. R.Akhmedov, E.Akhmedov. Perspective ecological safe technologies of burning of organic fuel with effective capture and useful utilisation of CO_2 . Proceedings of the 4th International Conference on Greenhouse Gas Control Technologies, 30 August – 2 September 1998, Interlaken, Switzerland, p. 735.

Poster Presentation
**DFT MODELING OF CO₂ UPTAKE AND DIMETHYL CARBONATE
FORMATION WITH METHOXYMETHYLSTANNANES**

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The interaction between CO₂ and metal atoms, surfaces, or complexes has been approached both by experimental and theoretical studies. The coordination of carbon dioxide to a metal center was considered as a key step for its transformation to useful organic products. Our experimental results on dialkyl carbonate synthesis from CO₂ and alcohol in the presence of dialkoxy-dibutylstannanes led us to examine the reaction pathway by DFT.

DFT calculations were performed to determine the energy of the reaction and to locate the transition state leading to the carbonation of the reactant. The ADF code has been used for this purpose, and a gradient-corrected exchange-correlation functional, namely the Perdew-Wang 91 one, has been retained for all the calculations. The calculated systems were Me₂Sn(OMe)₂, Me₃SnOMe, and the carbonato species Me₂Sn(OMe)(OCO₂Me), Me₂Sn(OCO₂Me)₂, [Me₂Sn(OMe)(OCO₂Me)]₂, Me₃Sn(OCO₂Me). Their structures have been characterized by vibrational analysis in the harmonic approximation, indicating a true minimum in case of no imaginary frequency, and a transition state in case of one imaginary frequency. The energy barrier for CO₂ insertion is low, <20 kJ mol⁻¹, and the carbonation is exothermic. The most stable compound was found to be the monocarbonated dimeric species, [Me₂Sn(OMe)(OCO₂Me)]₂, with bridging -OMe groups. Participation of these species to dimethyl carbonate formation will be discussed.

Keywords: Dimethyl carbonate, Methoxymethylstannane, CO₂, Reaction mechanism,
DFT calculations

Oral Presentation
SYNTHESIS OF DIALKYL CARBONATES FROM ALCOHOLS AND CO₂
UNDER SUPERCRITICAL CONDITIONS

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Dialkyl carbonates are currently produced by oxidative carbonylation of methanol, involving CO, and by the phosgene route. Using CO₂ instead of CO or COCl₂ constitutes an attractive alternative avoiding hazardous and toxic components. As a matter of fact, the industrial syntheses of urea, cyclic carbonates, salicylic acid, and methanol already involve CO₂ as a reactant. Nowadays, the development of new applications is of major interest from the point of view of CO₂ sequestration and within the scope of environmentally friendly reactions. Comparing CO₂ to CO and COCl₂ as a C₁-building blocks, the former has the obvious advantages to be non toxic, easy to transport and to store. However, the thermodynamic stability and kinetic inertness of CO₂ constitute serious drawbacks for its transformation/incorporation to organic molecules. Several ways of activation are currently under investigation; among them chemical catalysis offers a number of options. In this field, we are interested in the molecular design of catalysts for the formation of dialkyl carbonates from CO₂ and alcohols (eq 1).



We will present results on the mechanistic approach of dialkyl carbonate synthesis from alkoxybutylstannanes. The insertion of carbon dioxide into Sn-O bonds occurs at room temperature leading to Sn-OCO₂R species. For polyalkoxy derivatives, only one Sn-OR bond reacts with CO₂. Under catalytic conditions, only bis- and trisalkoxystannane derivatives produce dialkyl carbonates (selectivity = 100%). Pressure and temperature effects as well as reaction time were studied for dimethyl carbonate synthesis. The optimum temperature and pressure are 150°C and 200 bar, respectively; under these conditions, the reaction operates under *supercritical* CO₂. Intermediate organostannanes such as carbonated distannoxanes have been isolated from the reaction medium. The relevance of these species for dimethyl carbonate formation will be discussed, and DFT calculations will be presented.

Keywords: Dialkyl carbonate, Alkoxybutylstannane, Supercritical CO₂, Reaction mechanism, DFT calculations

Oral Presentation

Copolymerization of CO₂ and Cyclic Ethers

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That CO₂ could be copolymerized with cyclic ethers has been known since Inoue's groundbreaking work in 1969. This research plus subsequent work over the next two decades showed that one could catalyze the sequential insertion polymerization of CO₂ and various cyclic ethers to form relatively high molecular weight material. The catalysts employed were usually based on mixtures of dialkyl zinc compounds with various activators/promoters. Activities were lower than what was desired by industry for scale-up purposes, and the molecular weight distributions of the copolymers were usually broad.

During the mid-1980's Inoue's group showed that one could create a "single-site" type catalyst, here an aluminoporphyrin, that would generate copolymers of CO₂ and oxiranes with narrow molecular weight distribution, but at very slow rates. Darensbourg's group created a single-site type catalyst (a phenoxy-zinc) in 1994 that showed extremely high activity in the copolymerization of cyclohexene oxide (CHO) and CO₂. Finally, Coates (1999) generated an alkoxy zinc with β -di-imine ligands that exhibited phenomenal activity in CHO/CO₂ copolymerizations, and more remarkably, at very low CO₂ pressures.

In our lab, we have examined the use of sterically hindered aluminum compounds as catalysts for the copolymerization of CO₂ and oxiranes, with the goal of producing copolymers whose CO₂ content could be controlled and whose molecular weight distribution were less than 2.0. Further, in order to render the catalysts practical for generation of materials such as polyols (poly(ether-carbonate diols, Mw ~ 3000), they should tolerate the use of simple alcohols as chain transfer agents. We have found that sterically hindered aluminum compound readily support the copolymerization of CO₂ and ethylene or cyclohexene oxide, generating copolymers with narrow MWD's. For the case of propylene oxide, a 50:50 mixture of copolymer and simple cyclic propylene carbonate is produced. We have examined various strategies to reduce the propylene carbonate percentage through alterations to process temperature, CO₂:oxirane ratio, and through the use of co-catalysts. Finally, when one employs CO₂ as both the reactant and the solvent, it is important to remember that the phase behavior of the system can affect the outcome of the polymerization.

Oral Presentation
Photocatalytic Oxidation of Organic Compounds on Titania in Supercritical Carbon Dioxide

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Carbon dioxide is viewed as an environmental boon – in the context of replacing organic solvents that can result in air and water pollution. At the same time CO₂ is implicated as a major threat to the global environment – due to its greenhouse effect when released by the consumption of fossil fuels for energy production. Supercritical CO₂ systems are under development for applications in treating mixed and hazardous wastes. Another important application of supercritical carbon dioxide is in the area of cleaning electronic components, micro-devices, and other parts where the advantages of low viscosity and solvent properties have a high value. This work demonstrates that photocatalytic oxidation can be used to remove trace organic contaminants from carbon dioxide in the supercritical, liquid, and gas phases. This has applicability in processes where it is desirable to recycle the carbon dioxide in contaminant sensitive applications.

This poster reports results establishing that photocatalytic oxidation can be carried out in supercritical carbon dioxide. A system was designed and constructed so that the photocatalytic oxidation of organic compounds could be carried out in supercritical carbon dioxide. Prior to this work there were no reports of photocatalytic oxidation using titanium dioxide catalysts in supercritical fluids. The experimental system can operate at temperatures from 25-50 °C, pressures from 15-5000 psi, and with gas, liquid, and supercritical fluid phases. The concentration of organic solutes can be followed using on-line gas chromatography or UV-Vis spectroscopy. Experiments have measured the rates of oxidation of benzene, toluene, hexane, cyclohexane, and acetone in gas phase (80:20 N₂:O₂ and CO₂:O₂) and in supercritical CO₂. The concentration versus time data for the reactions can be fitted to a Langmuir-Hinschelwood model. Rates are lower in supercritical CO₂ than in the gas phase.

Poster Presentation
**PROCESS OF DIMETHYL CARBONATE SYNTHESIS USING
SUPERCRITICAL CARBON DIOXIDE :
STUDY AND MODELLING OF THE REACTING MIXTURE
FRACTIONATION**

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As part of a project for dimethyl carbonate (DMC) synthesis by direct methanol carbonation using supercritical CO₂, we have studied a semi-batch fractionation process for the CO₂/Methanol/DMC/Water mixture using supercritical CO₂. Water, which is co-produced, has a detrimental effect on a possible reversal of carbonation reaction, as well as on the good operation of the organotin catalyst. This implies that it is preferable to eliminate reaction products as the reaction proceeds, and led us to study the fractionation process implemented at the output of the reactor. This fractionation process has been studied and modelled in a semi-continuous mode.

It has been necessary to investigate the thermodynamic behavior of the reacting quaternary mixture. Operating conditions, as well as component characteristics, led us to choose the Soave, Redlich and Kwong equation of state coupled with the MHV2 mixing rules. The literature being free from experimental data for binary mixtures involving DMC, phase equilibrium experiments were carried out. The quaternary mixture fractionation has been experimentally operated with an extraction-separation pilot, commonly used for supercritical extraction. This process comprises an extractor used as a simple contactor, allowing an intimate contact between a mimicked Methanol/DMC/Water mixture and CO₂ entering the process. A constant feed flow rate of CO₂ is kept. The outgoing fluid undergoes a three successive depressurisation stages to recover the targeted components (DMC and water), then CO₂ and methanol may be recycled (Separex pilot, 200 cm³ contactor, three cyclonic separators).

Dynamic modelling has been developed to represent the mixture behaviour inside the process, and compared to experimental results. A simplified numerical approach used to solve dynamic mass balances has been proposed and validated in comparison with a rigorous resolution of the algebro-differential system of equations. The description of the process, based on the concept of theoretical stage, proved to be relevant to describe the mixture behaviour inside the contactor, but results for separators were less satisfying. Alternate descriptions of separator technology are proposed.

Keywords : Dimethyl carbonate, Supercritical CO₂, Phase equilibria, Dynamic modelling , Cyclonic separators, Fractionation

Poster Presentation
**SUPERCRITICAL FLUIDS AS REACTION MEDIA USEFUL TO MODULATE
PSEUDOMONAS CEPACIA LIPASE ACTIVITY IN TRANSESTERIFICATION
REACTIONS**

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It is well known that biocatalysed reactions in nonconventional media [1-3] (different organic solvents and supercritical fluids) are usually influenced by different physical parameters, for example, pressure, temperature, etc. The effect of pressure on the catalytic activity of enzyme catalysed reactions in supercritical fluids (SCFs) was first presented by Randolph [4] and Erickson et al. [5] showing reaction rates significantly enhanced near the critical point making the range of high compressibility, close to that point, the most interesting to be investigated. As is well known, the effect of pressure on reaction rate depends on the magnitude and the sign of the differences in volume between and the ground states for the reaction steps involved, i.e. the activation volumes for each step, ΔV^\ddagger . The reaction step, which proceeds through a reduction in volume, is accelerated by an increase in pressure and vice versa.

In this work we studied the performance of an immobilised lipase from *Psuedomonas cepacea* in the acetylation of (\pm)-1-phenylethanol, as model substrate, with vinyl acetate in supercritical and near-critical CO₂. We examined the effect of pressure on reaction rate, and lipase catalytic efficiency through estimation of the activation volumes of the processes. The study of kinetic mechanism of reactions has been also carried out.

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Poster Presentation

High-Pressure Phase Equilibria of Carbon Dioxide–Water–*n*-Butanol System

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Abstract

Due to the rapid developments of supercritical fluid technology in fields of polymers, medicines, materials, extraction and waste-treatments etc., the measurements of high-pressure phase equilibrium received much attention in recent years. These phase equilibrium data play an important role on the process design for many related chemical industries and supercritical fluid utilizations.

In this study, the phase equilibrium measurements for CO₂–*n*-butanol and CO₂–water–*n*-butanol systems were carried out with a novel phase behavior apparatus under 333.15–353.15 K and 50–130 bar. The accuracy and reliability of these measurements were first examined with previous reports. It showed that the experimental data obtained in this work were in good agreement with previous reports. From the phase equilibrium data of CO₂–*n*-butanol and CO₂–water–*n*-butanol systems, the phase diagrams for these systems were constructed. Furthermore, the theoretical calculations of phase behavior with equations of state were also proposed for comparison.

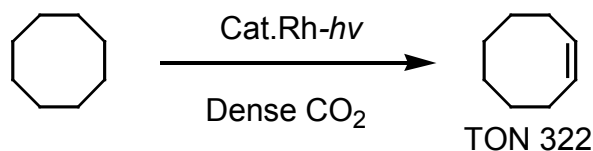
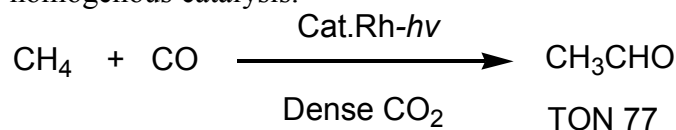
Keywords □ carbon dioxide, *n*-butanol, water, phase equilibrium, supercritical fluid.

Poster Presentation
Catalytic C-H Bond Activation by the $\text{RhCl(PMe}_3)_3$ - $h\nu$ System in Dense Carbon Dioxide

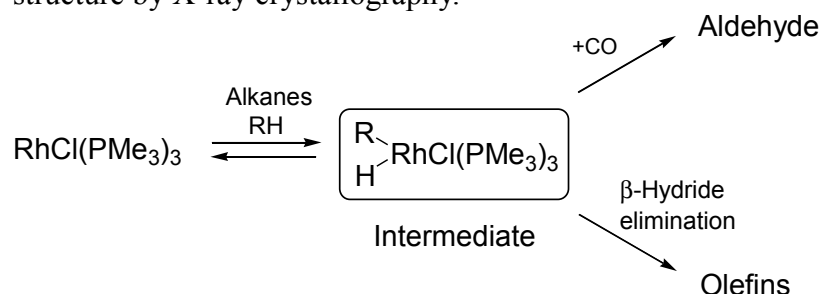
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A major problem concerning complex-catalyzed C-H bond activation is the lack of suitable solvents because most organic solvents are not tolerant under alkane activation conditions. We have achieved the methane carbonylation and alkane dehydrogenation by the $\text{RhCl(PMe}_3)_3$ - $h\nu$ system in dense carbon dioxide. Hence, dense carbon dioxide is an efficient reaction medium for C-H bond activation by homogenous catalysis.



As for the mechanism, we investigated the photo-reaction of benzene and $\text{RhCl(PMe}_3)_3$ at a molecular level. The reaction proceeded smoothly to give the corresponding rhodium(III) complex with phenyl and hydride groups as judged by the ^1H and ^{31}P NMR data. The observation of a strong IR peak at 2036 cm^{-1} was another support for the Rh-H bond. Finally, we have determined the complex structure by X-ray crystallography.



Acknowledgment. This study was supported by Industrial Technology Research Grant Program in 2000 from the New Energy and Industrial Technology Development Organization (NEDO) of Japan.

Poster Presentation

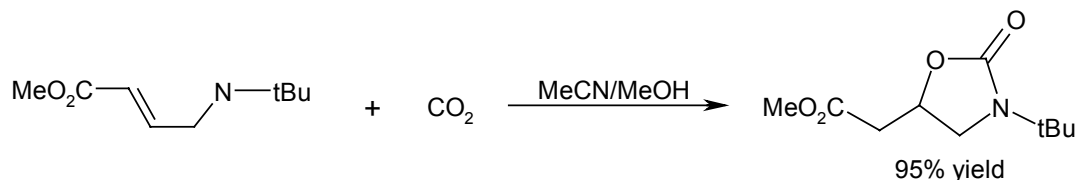
1,3-Oxazolidin-2-one ring formation from carbon dioxide and N-alkyl- γ -aminocrotonate under homogeneous and supercritical conditions

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We have recently shown that the catalytic use of superbases such as N-tri-, tetra- and penta-alkyl-substituted guanidines allows the direct introduction of carbon dioxide in N-alkyl-substituted prop-2-yn-1-amines¹ under mild conditions in acetonitrile to give fair to excellent yields of N-alkyl-5-methylene-1,3-oxazolidin-2-ones. The use of strong bases able to stabilize the intermediate carbamate anion was the key for the success of this reaction. Subsequently we have shown that carbon dioxide and carbon monoxide react in sequence in an intramolecular carboxy-carbonylation reaction with N-alkyl-substituted 1,1-dialkylprop-2-yn-1-amines under the catalytic action of palladium iodide-potassium iodide in alcohol in the presence of oxygen², giving two (E and Z) 5-(alkoxycarbonyl)methylene-3,4,4-trialkyl-1,3-oxazolidin-2-one stereoisomers.

We now report new developments concerning the reaction of carbon dioxide with N-alkyl- γ -aminocrotyl derivatives. Thus, for example, methyl N-tert-butyl- γ -aminocrotonate (1 mmol) in MeCN/MeOH (2 ml 1:1) and CO₂ (40 bar) were caused to react in the absence of catalyst at 80 °C for 24 h. Methyl N-tert-butyl-1,3-oxazolidin-2-one-5-acetate, corresponding to 5-exo-dig ring closure in agreement with Baldwin's rules, was obtained in excellent yield according to eqn:



The reaction showed to be sensitive to the nature of the solvents. Analogous results were obtained in supercritical CO₂ in the absence of other solvents. The effect of the nitrogen substituents and the different crotyl derivatives of the starting substrate have been investigated.

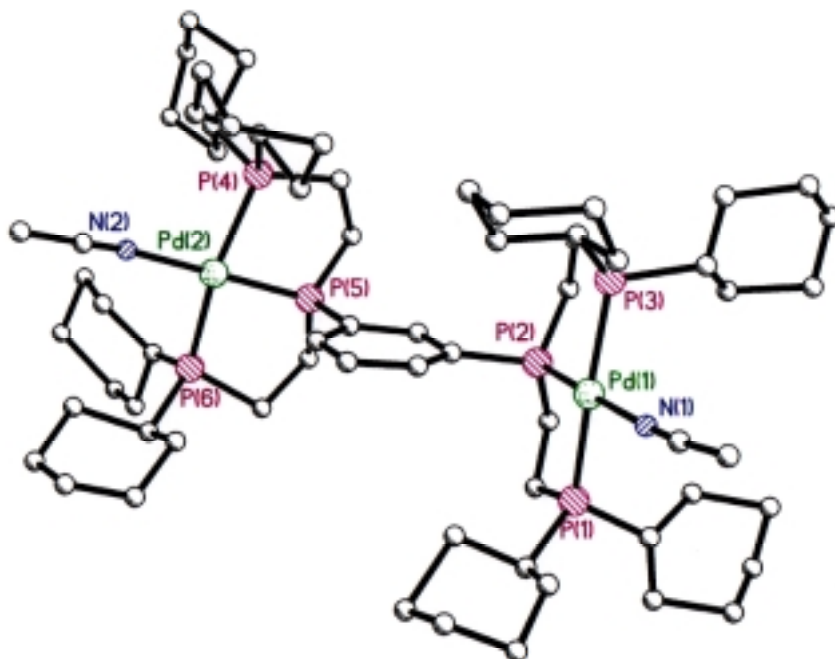
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Poster Presentation
RAPID THROUGHPUT STUDIES OF BIMETALLIC CO₂ REDUCTION CATALYSTS

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This poster describes a rapid throughput approach to the development of bimetallic CO₂ reduction catalysts. In these studies, a series of bridging ligands containing two separate triphosphine units were prepared that are capable of binding two metals. This structural feature was selected because of our previous demonstration that [Pd(triphenylphosphine)(CH₃CN)](BF₄)₂ catalysts are effective CO₂ reduction catalysts. The synthesis of these ligands will be presented. These ligands have been used to prepare a library of compounds that include pure homobimetallic compounds and mixtures of homobimetallic and heterobimetallic complexes. Selected members of this library were studied by ³¹P NMR spectroscopy to confirm that the synthetic procedures were indeed capable of producing the desired bimetallic complexes. This library was then screened using a sixteen channel multipotentiostat to identify initial hits. Those compounds that showed significant catalytic activity were evaluated further using standard electrochemical techniques. The compound showing the highest activity was a homobimetallic Pd complex that has been independently synthesized. An X-ray diffraction study of this complex has been completed and confirms its bimetallic nature. Kinetic studies of this complex are underway and will be presented. Our results support the feasibility of using the rapid throughput approach to the development of electrocatalysts for CO₂ reduction.



Oral Presentation
The CO₂ Technology Platform: Surfactants for Increased CO₂ Utility

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The coming years should find carbon dioxide used in an ever-increasing number of industrial applications, including materials production, cleaning protocols, extractions, and coatings. Many such processes will involve the use of surfactants, which have greatly enhanced the versatility and potential of CO₂ as a solvent by enabling the dispersion of otherwise insoluble components. Through judicious choice of surfactant, it is possible to utilize CO₂ as a medium for purposes ranging from the preparation of uniform, micrometer-sized polymer particles, to the formation of water-in-CO₂ microemulsions. Continued progress toward the application of CO₂/surfactant systems is dependent upon further advances in our fundamental understanding of surfactant behavior in CO₂, such as the impact of solvent density on block copolymer micellization, and the effects of altering surfactant structure on self-assembly. Here we describe how a variety of aspects of CO₂/surfactant systems are being approached in our laboratory, though the combination of synthetic and physical methods.

Oral Presentation

Direct Synthesis of Acetic Acid from CO₂ and CH₄ over Supported Pd and Rh Catalysts

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The effective utilization of CO₂ and CH₄ would be far more attractive in recent years in view of more and more serious global greenhouse effect. In this paper, the supported Pd and Rh catalysts have been preliminarily investigated to catalyze the direct conversion of CO₂ and CH₄ to acetic acid through the two-step isothermal reaction sequences. Acetic acid, as one of the target products, is more useful and convenient for the direct conversion of CO₂ and CH₄, which, however, is thermodynamically unfavorable. In the sequences, the catalyst was first exposed to CH₄ to form surface carbonaceous species M-CH_x, then CO₂ introduced was inserted the surface species, after hydrogenation, to produce acetic acid. By such a two-step route, we tried to circumvent the thermodynamics of the reaction. The outlet gases from the micro-reactor were detected by the gas chromatography, and the liquid products by the ion chromatography.

Recent results showed that following this two-step route could overcome the thermodynamic limitation. The supported Pd catalysts were more active than the supported Rh ones; SiO₂(especially superfine SiO₂) was the optimum supporter, the catalysts supported on TiO₂ and zeolite could also produce formic acid as well as superfine SiO₂; 170° and 200° were the better reaction temperatures; The thermal analysis and transmission electron microscope showed the distinguishing advantage that no apparent deactivation resulted from carbon deposition after the successive reaction cycles.

Keywords carbon dioxide, methane, acetic acid, direct conversion, two-step reaction, supported catalyst

Oral Presentation
The Global Carbon Cycle and its Role in Climate Change

Ed Dlugokencky

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Arrhenius was the first to quantify the role of varying amounts of atmospheric CO₂ on climate in the late-19th century. His work relied heavily on a published description by Högbom of the geochemical processes that controlled the abundance of atmospheric CO₂. Though both men realized that combustion of fossil fuels was adding to the atmospheric abundance of CO₂, they did not foresee the more than factor of 10 increase in fossil fuel combustion during the 20th century that has led to serious concerns about future climate.

Measurements of CO₂ in air bubbles trapped in ice cores show that for more than a 1000 years prior to industrialization, the atmospheric abundance of CO₂ was relatively constant at 280 ppm (parts in 10⁶ by mole fraction). This implies that the exchange of CO₂ among those reservoirs accessible on time-scales of about a year (atmosphere, biosphere, and surface ocean) was at steady-state. Rates of exchange of CO₂ with the lithosphere, deep ocean, and fossil reserves were too slow to be important. Widespread use of fossil fuels has perturbed the atmospheric CO₂ abundance from steady state; $\sim 7 \times 10^{15}$ g C (as CO₂) will be emitted into the atmosphere in 2001 from fossil fuel combustion and cement production. Based on 40 years of measurements of the atmospheric CO₂ abundance, we know that about half of the emitted CO₂ remains in the atmosphere while the other half is taken up by the oceans and the biosphere. The relative contribution of each sink is important for policy: CO₂ that reaches the deep oceans is removed from the atmosphere for centuries. CO₂ taken up by the biosphere is much more susceptible to return to the atmosphere due to human and climate perturbation of this sink. Accurate determination of the partitioning of fossil CO₂ between ocean and biosphere reservoirs is based on a combination of modeling, measurements of the isotopic composition of CO₂, and measurements of the atmospheric abundance of O₂. Current best-estimates of this partitioning suggest about 2/3 of the sink is in the ocean and about 1/3 in the biosphere. The combination of observations and models is not yet good enough to partition the biospheric sink regionally with a high degree of certainty.

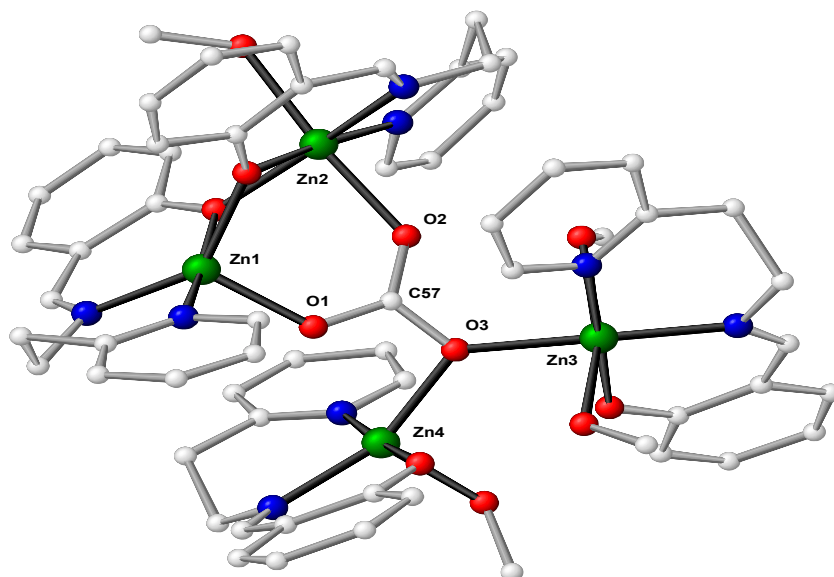
Combusting all known fossil reserves could result in temporary atmospheric CO₂ abundances greater than 2000 ppm, with subsequent radiative forcing of $\sim 12 \text{ W m}^{-2}$ (compared with 2.5 W m^{-2} from all greenhouse gases in 2000). Such high CO₂ values have the potential to exhaust the buffering capacity of the surface oceans before the atmospheric CO₂ abundance begins to decrease on longer time scales as carbon is cycled into the deep oceans.

Oral Presentation
ZINC SCHIFF BASE COMPLEXES FOR CO₂ FIXATION:
ENZYMATIC MODELS OF CO₂ REACTIONS

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Zinc Schiff base complexes capable of fixing CO₂ are the subject of our current study. We report the synthesis, characterization and reactivity of new tetra- and dimetallic zinc carbonate and bicarbonate complexes and their precursors. The derivative shown was obtained by the reaction of a water complex with CO₂ in boiling methanol. Depending on a small change of the pH value, this reaction is reversible. Furthermore, we describe the synthetic routes to zinc carbonate complexes with different coordination mode.



Oral Presentation
**STRUCTURAL AND MECHANISTIC DIVERSITY OF PROCARYOTIC
CARBONIC ANHYDRASES**

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Recently, it was established that carbonic anhydrases are common in phylogenetically and metabolically diverse procaryotes portending broad physiological roles for this enzyme. Two independently evolved classes are prevalent in procaryotes, the beta class (plant-type) and the recently discovered gamma class. The crystal structure of the homotrimeric gamma enzyme from *Methanosarcina thermophila* reveals a novel left-handed beta helical fold. The active site zinc is ligated by two histidines from one subunit and a third histidine from the adjacent subunit. Residues in the active site have no analogs to catalytic residues identified in the well studied alpha class carbonic anhydrases that predominate in mammals. A zinc-hydroxide mechanism of catalysis is inferred from stopped flow kinetic data. Overexpression of the gamma enzyme in *Escherichia coli* and kinetic analyses of replacement variants combined with biochemical characterizations and crystal structures with bicarbonate bound has identified residues essential for activity. Replacement of the zinc with iron leads to a four-fold increase in activity suggesting the iron form is physiologically significant and further identifies a novel function for iron in nature. Kinetic analysis of the beta carbonic anhydrase from *Methanobacterium thermoautotrophicum* also establishes a zinc-hydroxide mechanism for this enzyme. The crystal structure has been obtained with the substrate HEPES buffer molecule which suggests residues required for proton transport out of the active site subsequent to ionization of the zinc-bound water. Overexpression and kinetic analyses of replacement variants has identified residues essential for activity. Physiological roles of these enzymes will also be discussed.

Poster Presentation
**Supercritical fluid extraction of polyphenols from
by-products of potato industry**

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ABSTRACT

Potato tubers contain a large number of phenolic compounds with the largest proportion found in the skin and in the periderm layer near to it. Among them, the most representative is the chlorogenic acid, which content ranges from 5 to 50 mg/kg of dry matter. Other phenolic substances include phenolic acids (caffeic, ferulic, protocatechic), monohydric phenols (tyrosine, coumaric acid) and flavonoids (flavones, anthocyanins). Due to their antioxidant power, potato phenolic compounds are considered relevant to prevent many human diseases and to promote the quality of life. These natural antioxidants can be also extracted from potato by-products and used in food industry to prevent the decay by peroxidation of lipid bearing foods. The recovery of these compounds, characterized by a delicate molecular structure and by a general thermo-sensibility, requires however the use of mild extraction technologies, in order to preserve their antioxidant power. In such a contest, the extraction with supercritical fluids (SCF) is of great interest for the possibility to work at low temperature and to pilot the solvent properties of the SCF.

On this basis, a research was developed with the aim to maximize the extraction yields, by the optimization of working conditions, and to characterize the phenolic extracts under a functional point of view. The extraction was developed using a pilot plant which allows the recovery and the subsequent recycling of the solvent (SC-CO₂). The optimization of extraction parameters (temperature, pressure and SCF flow rate) was carried out using a kinetics approach based on Fick law. This approach also uses the equation introduced by Chrastil (1982) to correlate the maximum extraction rate (assumed as a measure of solvent power of supercritical fluid vs the antioxidant compound) to temperature and relative density of SCF.

As the first part of the experimentation showed that pure SC-CO₂ is a poor solvent for these polar compounds and that water is not suitable as co-solvent being unable to generate a homogeneous phase with SC-CO₂, ethanol (EtOH) was considered and tested as co-solvent. It was used coupled to SC-CO₂ in a ratio varying from 20 % to 100% (w/w). In the experiment runs EtOH showed a complete miscibility with SC-CO₂ and was quantitatively recovered in the separator. SCF-extractions were carried out with a working pressure varying from 20 to 70 MPa and with a temperature changing from 40 to 80 °C; the flow rate of SC-CO₂ was maintained constant and equal to 10 kg/hour.

The values of the kinetic constants obtained showed that high percentages of EtOH are needed to obtain a significant extraction of polyphenolic fraction. The paper reports the kinetics of the extractions, knowledge of which allows the optimization of working parameters and the determination of process yields. On the basis of the results obtained, a three steps SCF-extraction process is tentatively proposed for processing potato by-products on an industrial scale.

Poster Presentation

The Uses of Carbon Dioxide in Supercritical Technology Researches in Brazil

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The high solubilization power of the supercritical fluids at elevated pressures and low temperatures makes the supercritical extraction an attractive method to the fractionation of the paraffinic hydrocarbons, separation and purification of the gases in the petroleum industry and in the development of actual technologies of enhanced oil recovery.

Supercritical fluids also can be attractive solvents in difficult separations. In food processing, carbon dioxide is the solvent of first choice because of its advantages like low cost, atoxicity, lower critical temperature and high volatility.

The use of supercritical CO₂ for the extraction and purification of natural products from many raw material has been extensively studied for several years. It has a number of processing advantages over hexane conventional extraction methods which include the absence of residues of the organic solvent and the thermal degradation of the natural products.

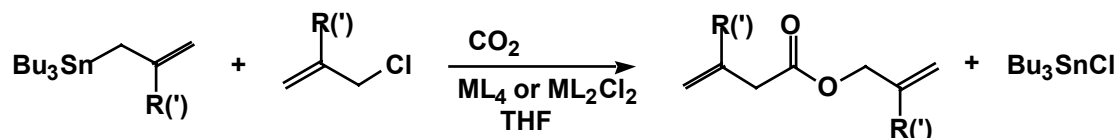
In our research developments in Brazil, the uses of carbon dioxide reach many different areas, like supercritical extraction of natural products and in the petroleum are, specifically in enhanced oil recovery.

The objective of this work is to show how carbon dioxide can contribute in the improvement of the development and industrial design of a supercritical extraction unit. For this purpose, the CO₂ is utilized initially in many experimental works like phase equilibrium and solubility measurement and in the fractionation, separation and purification of many natural products native of Brazil in countercurrent columns and extractors.

Poster Presentation
METAL-PROMOTED CARBOXYLATIVE COUPLING OF
ORGANOMETALS AND ORGANIC ELECTROPHILES

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Our studies of carbon dioxide activation have recently sought to develop new catalytic, carbon-carbon bond-forming reactions of CO₂. Following the discovery that allyl stannanes are efficiently converted to tin carboxylates upon reaction with CO₂ in the presence of Pd(PPh₃)₄ [1], we recently developed a carboxylative coupling process in which allyl halides, allyl stannanes and CO₂ undergo carboxylative coupling to produce allyl butenoate esters catalyzed by Pd and Pt complexes [2].



For example, allyl chloride and allyltributyl stannane are converted to propenyl butenoate in excellent yield under 30-40 atm CO₂ in THF at 70 °C in the presence of 5 mol% Pd(PPh₃)₄. *In situ* NMR and IR experiments have provided insight into the species present under catalytic conditions and reactivity studies of prospective reaction intermediates and model compounds form the basis for a proposed reaction mechanism. Our progress in extending the scope of this reaction beyond allylic substrates and to other organometals and catalysts will be presented.

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Oral Presentation
**MECHANISTIC STUDY OF CO₂ PHOTOREDUCTION IN Ti SILICALITE
MOLECULAR SIEVE**

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CA 94720

A recent heterogeneous approach to CO₂ photoreduction employs micro or mesoporous silicates containing Ti centers in the framework (Anpo, 1997, 1998, 2000). Reactions are conducted in aqueous suspensions or on molecular sieve loaded with gaseous CO₂ and H₂O. Efficiencies of CO₂ reduction to methanol or methane in these porous materials by UV light are found to be enhanced compared to semiconductor TiO₂ particles. This effect is attributed to the presence of isolated, tetrahedrally coordinated Ti centers. However, the mechanism of CO₂ photoreduction in Ti framework substituted sieves remains unknown as monitoring of the reaction has thus far been conducted by gas-chromatographic analysis of the desorbed final products CH₃OH and CH₄. Knowledge of the elementary steps of this reaction at the gas-micropore interface would furnish crucial insight for the selection of new framework metals and porous structures that may afford activation of CO₂ at longer photolysis wavelengths. We have therefore conducted an in-situ FT-infrared spectroscopic study of the photoreduction of CO₂ in TS-1 sieve by using CH₃OH as electron source. Methanol was chosen as donor because the 2-electron transfer reaction of CO₂ and CH₃OH involves endoergicities that, in principle, render the reaction accessible by visible photons.

TS-1 synthesized and characterized in our laboratory (including characterization by XANES spectroscopy) was loaded with CO₂ and CH₃OH gas, and photo-reaction initiated by 266 nm excitation of the Ti^{+IV}-O^{+II} - > Ti^{+III}-O^{-I} LMCT transition. FT-infrared difference spectroscopy revealed growth of HCO₂H, CO and HCO₂CH₃. No reaction was observed in neat silicalite sieve, which confirms that the Ti centers are acting as chromophores and redox initiators. The origin of the products was elucidated by photolysis experiments with C¹⁸O₂, ¹³CO₂, and ¹³CH₃OH. Carbon monoxide, which escaped instantly into the gas phase, was quantified by high resolution FT-IR measurements and found to originate from CO₂. However, the induction behavior of its growth indicates that it is produced by secondary photolysis of HCO₂H. We conclude that CO₂ photoreduction at LMCT-excited framework Ti centers results in single photon-induced 2-electron reduction of CO₂ to HCO₂H. Concurrently, CH₃OH is oxidized to CH₂=O, which undergoes Tishchenko dimerization to yield HCO₂CH₃. The key result of this study is that C-H bond formation occurs in the initial steps of the photoactivation of CO₂ at the gas-solid interface, and O atom abstraction does not take place. The result constitutes the first insight into the primary steps of CO₂ photoreduction in a Ti molecular sieve. The presentation will focus on in-situ studies of the system with static spectroscopy and recent progress of recording transient intermediates in these framework sieves by time-resolved FT-IR spectroscopy.

Oral Presentation
**TRANSIENT FTIR STUDY OF RHENIUM COMPLEXES
IN PHOTOCHEMICAL CO₂ REDUCTION**

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The tricarbonyl rhenium complex with the general formula, *fac*-Re(α -diimine)(CO)₃X (X = halide, solvent, alkyl, monodentate phosphine, CO, etc), has been shown to be a photocatalyst for the reduction of CO₂. The mono- and di-reduced species, Re^I(bpy^{•-})(CO)₃ and [Re(bpy)(CO)₃]⁻, respectively, are proposed as intermediates which react with CO₂.

We have used transient FTIR to study the reaction mechanism involving the mono-reduced species, which is produced either by reductive quenching of *Re(dmb)(CO)₃X (dmb = 4,4'-dimethyl-2,2'-bipyridine, X = Cl⁻ or solvent) or by photolysis of Re(dmb)(CO)₃(Et). Transient FTIR of the excited state, *Re(dmb)(CO)₃X (X = Cl⁻ or solvent), shows a significant shift (20 to 80 cm⁻¹) of the CO vibrational frequencies to higher energy, which is consistent with the formation of the ³MLCT state. The reductive quenching reactions of *Re(dmb)(CO)₃Cl and *Re(dmb)(CO)₃(CH₃CN)⁺ by triethylamine produce [Re(dmb)(CO)₃Cl]⁻ and Re^I(dmb^{•-})(CO)₃, respectively. A transient FTIR study of the photolysis of Re(dmb)(CO)₃(Et) indicates clean cleavage of the Re-Et bond, forming Re^I(dmb^{•-})(CO)₃. Under an Ar atmosphere the mono-reduced complex produces two species with bands at 1990, 1947, ~1870, and 1855 cm⁻¹ and 2021, 1919, and ~1870 cm⁻¹. Comparisons with IR spectra obtained by sodium reduction of Re(dmb)(CO)₃(OTf) (OTf = trifluoromethanesulfonate) suggests that the former is a [Re(dmb)(CO)₃]₂ dimer. Under a CO₂ atmosphere the mono-reduced complex produces the formato complex, Re(dmb)(CO)₃(OC(O)H), and the carboxylate complex, Re(dmb)(CO)₃(COOH). When small amounts of water are present, a yellow precipitate is obtained during the photolysis. The precipitate was identified as a bicarbonato complex, Re(dmb)(CO)₃(OC(O)OH).

This study suggests that Re^I(dmb^{•-})(CO)₃ reacts to form either a dimer ($k = 20 \text{ M}^{-1} \text{ s}^{-1}$) or a CO₂ adduct ($k < 1 \text{ M}^{-1} \text{ s}^{-1}$). Due to the sluggishness of these reactions very small amounts of water can intercept Re^I(dmb^{•-})(CO)₃.

This research was carried out at Brookhaven National Laboratory under contract DE-AC02-98CH10886 with the U.S. Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences.

Poster Presentation
**OXYGEN-BLOWN COMBUSTION IN ADVANCED COMBINED AND MIXED
CYCLES WITH ULTRA-LOW CO₂ EMISSION**

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ABSTRACT

Continuous development of the world economy involves a substantial increase of the emission of carbon dioxide resulting from the combustion of fossil fuels. This increase in the concentration of carbon dioxide and other greenhouse gases in the atmosphere may enhance the green house effect. As a consequence the climate on earth may change considerably, causing environmental degradation. In order to limit the risks of climatic change, the man-made carbon dioxide emissions have to be reduced.

To reach this aim, the methodologies proposed up to now are:

1. CO₂ removal process treating the products of combustion from fossil fuel power plants and next storage of the removed gas in suitable places.
2. using of semi-closed cycles where the working fluid is prevalently CO₂: in this case it's necessary a combustion with pure oxygen generated in an air separation unit. The CO₂ excess, produced in the combustion process, is totally captured and it's possible to obtain a zero emission system.
3. "decarbonize" the fuel to produce hydrogen.

The AMC is an advanced mixed cycle with high conversion efficiency. Its plant lay-out consists of a reheat gas turbine with steam injection in the first combustion chamber, a steam turbine for steam expansion before its injection, a heat recovery boiler for superheated and resuperheated steam generation and an atmospheric separator for water recovery from exhaust gas mixture. The thermodynamic performance of this cycle had been investigated in previous papers. The main result was that this cycle showed relevant performance, regarding both thermodynamical and economic aspects, when equipped with systems to abate carbon dioxide emission by exhaust gas treatment (chemical absorption). In fact it is able to achieve very limited CO₂ emissions (0.04 kg/kWh), converting thermal power from fuel to electrical power at an efficiency level of about 50% and increasing its electricity production cost by about 20%.

In this paper we want to investigate the same cycle, but considering, this time, the second option, mentioned above, in order to obtain a zero-CO₂ emission plant. This objective can be pursued by adopting an oxidizer different from air, i.e. the oxygen. In this case the power plant must be integrated with an air separation unit (ASU) that must give the quantity of oxygen at the necessary purity. So the working fluid becomes a gaseous mixture of CO₂ and H₂O; after heat recovery and water condensation, part of the exhaust gas, highly concentrated in CO₂, must be recirculated at the inlet compressor and the other part can be extracted, compressed and liquefied for a next storage.

In this paper our attention will be paid to:

- ASU analysis in order to determine the energetic integration between this unit and the power plant;
- CO₂ LP analysis in order to determine the energetic integration between the CO₂ liquefaction plant and the power plant;
- thermodynamical optimization of the cycle, due to the change of the working fluid, in order to maintain high conversion efficiency with no CO₂ emissions.

Moreover in this paper we have the aim to compare performance of this mixed cycle with that of a combined cycle, based on a semi-closed gas turbine cycle using CO₂ as the working fluid and a combustion with pure oxygen generated in an air separation unit: the comparison is obviously developed under the same numerical assumption.

Oral Presentation

Synthesis and Properties of *fac*-Re(dmbpy)(CO)₃CHO (dmbpy = 4,4'-dimethyl-2,2'-bipyridine), a Possible Intermediate in Reductions of CO₂ Catalyzed by *fac*-Re(dmbpy)(CO)₃Cl

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Photo- and electrochemical reductions of carbon dioxide catalyzed by *fac*-Re(N-N)(CO)₃Cl (N-N = 2, 2'-bipyridine, 4,4'-dimethyl-2, 2'-bipyridine) lead to carbon monoxide and formate.¹ Previously, one possible route to formate was thought to involve an intermediate metallocarboxylic acid, *fac*-Re(N-N)(CO)₃COOH. Decarboxylation of the acid to *fac*-Re(N-N)(CO)₃H followed by CO₂ insertion into the metal hydride bond could provide formate whereas dehydroxylation would yield CO. We recently prepared and characterized one of the acids,² *fac*-Re(dmbpy)(CO)₃COOH, and studied its thermolysis reactions.^{2,3} However, these reactions do not provide formate, even when conducted in the presence of added CO₂. An alternate proposal, that formate might be generated in the catalytic systems from reactions of intermediate formyl complexes, has been suggested by us^{2,3} and others.⁴ We have now prepared and characterized one such formyl complex, *fac*-Re(dmbpy)(CO)₃CHO, and studied its reactions in the presence of CO₂ and in the presence of the corresponding metallocarboxylic acid. The results of these experiments will be presented.

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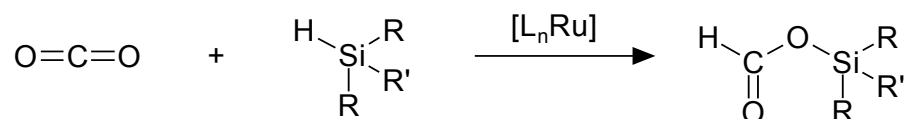
Oral Presentation
Atmospheric Pressure Hydrosilylation of Carbon Dioxide

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The chemistry of carbon dioxide as an alternative source of carbon for organic syntheses has attracted considerable interest in the last decades. The present study focuses on the selective synthesis of formoxysilanes which are possible building blocks for silicone polymers. The utilization of transition metal catalysis for the hydrosilylation of carbon dioxide has been reported to produce formoxysilanes of the type $R_3Si(OOCH)$.¹⁻⁴ Most recently, certain ruthenium complexes have been shown to act as very efficient catalyst for this synthesis.⁵



Results will be presented concerning hydrosilylation at atmospheric pressure and optimization of the reaction conditions and will be compared to high pressure syntheses. Data from spectroscopic investigations, kinetic measurements and calorimetric test will be given and discussed in detail.

The authors like to thank the Helmholtz-Gesellschaft (Germany) and the Max-Planck-Gesellschaft (Germany) for financial support.

¹ Koinuma, H.; Kawakami, F.; Kato, H.; Hirai, H. *J. Chem. Soc. Chem. Comm.*, **1981**, 213.

² Süss-Fink, G.; Reiner, J. *J. Organomet. Chem.*, **1981**, 221, C36.

³ Eisenschmid, T.C.; Eisenberg, R.; *Organometallics* **1989**, 8, 1822.

⁴ Jessop, P.G.; *Top. Cat.* **1998**, 5, 95.

⁵ Jansen, A.; Pitter, S. *Organometallics*, **2000**, 19, 135.

Poster Presentation

Avoidance of Carbon Dioxide Release by Combining Metal Oxide Reduction with Methane Partial Oxidation in a Thermo-neutral Process

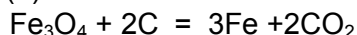
M. Halmann¹, A. Frei², and A. Steinfeld^{2,3}

¹Weizmann Institute of Science, Rehovot 76100, Israel

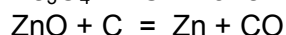
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³ETH-Swiss Federal Institute of Technology, CH-8092 Zurich, Switzerland

The current industrial production of metals from their ores features energy-intensive carbothermic processes that proceed at elevated temperatures, releasing about 10% of the annual world anthropogenic CO₂ (1).

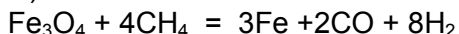


$$\Delta H_{298\text{K}} = 331 \text{ kJ mol}^{-1}$$

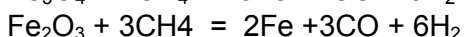


$$\Delta H_{298\text{K}} = 240 \text{ kJ mol}^{-1}$$

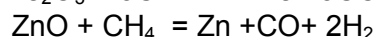
The use of natural gas (NG) as the reducing agent combines in a single process the reduction of metal oxides with the reforming of methane for the co-production of metals and syngas, while preventing the discharge of CO₂ (1-3).



$$\Delta H_{298\text{K}} = 976 \text{ kJ mol}^{-1}$$

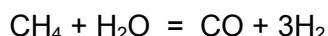


$$\Delta H_{298\text{K}} = 717 \text{ kJ mol}^{-1}$$

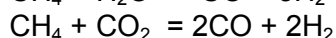


$$\Delta H_{298\text{K}} = 315 \text{ kJ mol}^{-1}$$

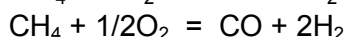
However, such reactions are also extremely endothermic, requiring an external energy source. Concentrated sunlight is one potential CO₂-free energy source, but would require a hybrid solar/fossil fuel plant for continuous operation. The thermo-neutral production of syngas has been achieved by combining the endothermic CH₄ reforming by H₂O or CO₂ with the exothermal partial oxidation of CH₄, using rare-metal catalysts (4-6).



$$\Delta H_{298\text{K}} = 206 \text{ kJ mol}^{-1}$$



$$\Delta H_{298\text{K}} = 247 \text{ kJ mol}^{-1}$$



$$\Delta H_{298\text{K}} = -36 \text{ kJ mol}^{-1}$$

In the proposed metallurgical process, the endothermic reduction of metal oxides is combined with the exothermic partial oxidation of methane, to co-produce metals and syngas in a thermo-neutral reaction. The stoichiometry for achieving thermo-neutrality and the corresponding equilibrium composition was computed for the temperature range 300-1500K, and for the metal oxides ZnO and Fe₂O₃. These reactions were further studied experimentally by thermogravimetry measuring the weight loss of the metal oxide, coupled to gas chromatography for determining the disappearance of CH₄ and O₂, and the appearance of H₂, CO, and CO₂, in a set-up previously described (3). For the reduction of ZnO, the reaction was performed at 1400K under a gas flow of Ar containing 3.9% O₂ and 5.5% CH₄, resulting in the complete reduction of ZnO to Zn(g) within 10 min, producing H₂, CO, and CO₂ in concentrations of 4.2, 2.4, and 1.4 volume %, respectively. Similarly, the reduction of Fe₂O₃ to Fe at 1400K under argon containing 3.9% O₂ and 5.5 % CH₄ was complete within 35 min, forming H₂, CO, and CO₂ in concentrations of 3.1, 2.5, and 1.4 volume %. For both reactions, the partial oxidation of methane under these conditions did not require added catalysts. The metals formed presumably catalyzed the reaction.

The proposed combined processes may be performed in an auto-thermal reactor under adiabatic conditions, and could potentially provide an economic incentive for achieving a significant decrease in carbon dioxide release in the metallurgical industry (6).

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Poster Presentation
Application of High Pressure to Photocatalytic Carbon Dioxide Reduction
Using Rhenium Complexes

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Rhenium bipyridine complexes have received a great deal of attention because they can act as photocatalysts for the CO₂-to-CO reduction by visible-light irradiation in the presence of an amine. The catalytic systems have unique features such as high chemical specificity and capability of the two-electron-transfer mediation without the assistance of any cocatalyst. Among the reported catalysts, phosphite-containing complexes show high quantum yields of CO formation.^{1,2} However, the catalysis is not so stable that the turnover number of CO formation reaches only 7-8 as maximum. The past reports mainly focused on the chemical structure to improve the catalysis. As another approach, change of CO₂ pressure is of interest because the high pressure may raise the reactivity of catalyst towards CO₂. The conventional reaction system consists of two phases, i.e. CO₂-saturated organic solvent phase containing the catalyst and amine, and CO₂-gas phase of normal pressure over it. Herein we report the photocatalytic CO₂ reduction in high-pressure one-phase system (high pressure CO₂ liquid without a organic solvent) using CO₂-soluble rhenium complexes.³ Furthermore, we report the CO₂ reduction in high-pressure two-phase system (high pressure CO₂ gas / liquid solvent) using several rhenium complexes and the results are compared with those of conventional normal pressure system.⁴

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Oral Presentation

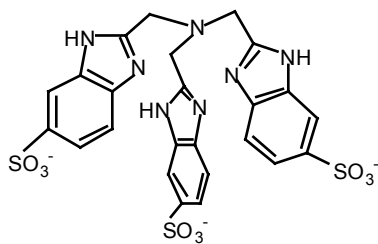
CO₂-Encapsulated Clathrate Hydrate Formed by Sulfonate-Assisting Hydrogen Bonds and Template Contribution from Helper Species of Zinc(II)

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The CO₂-encapsulated clathrate hydrate was formed, under a room temperature and atmosphere, by sulfonate-assisting hydrogen bonds among water molecules, where the geometry of the three sulfonate groups in zinc complex with nitrilotris(2-benzimidazolylmethyl-6-sulfonate) L1, was controlled by coordination of Zn²⁺.

The recovery of encapsulated CO₂ from the above hydrate was much more efficient than the case of saturated solution of CO₂(aq) and HCO₃⁻(aq). Because it is impossible to less than the saturated concentration. The sulfonate-assisting clathrate hydrate of CO₂ may be applied to the effective recovery of CO₂ from the view of both environmental earth and utilization.



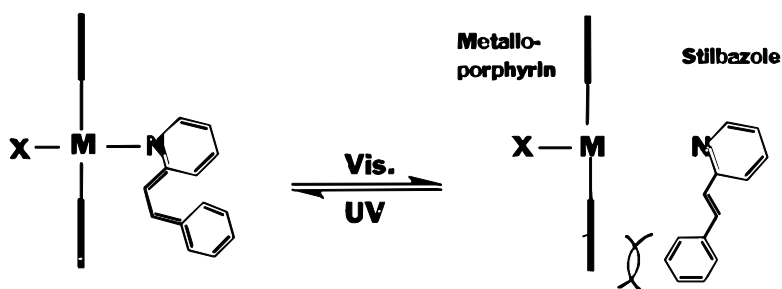
L1

Oral Presentation
**Reaction of Carbon Dioxide and Epoxide Controlled
by Light with Metalloporphyrin-Base System**

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A molecular switch system was developed for the control of carbon dioxide-epoxide reaction by light. Such system should consist of three parts: Reaction site, reaction control site, and photocontrol site. In view of the fact that the isomerization of olefin plays a central role in some photobiological processes, we selected the system consisting of metalloporphyrin and stilbazole as the components. Stilbazole is known to undergo the trans \rightarrow cis isomerization upon UV irradiation and the reversion by visible light via the complexation with metalloporphyrin. Based on this concept, we succeeded in the reversibly photocontrolled 'on-off' reaction of carbon dioxide and epoxide to form cyclic carbonate, catalyzed by aluminum porphyrin in the presence of a stilbazole as a coordinating ligand, induced by its photoisomerization.



Oral Presentation

Effective Synthesis of Ethanol by Catalytic Hydrogenation of CO₂ Using Ru₃(CO)₁₂-Co₂(CO)₈-LiBr-Bu₃PO System

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Catalytic hydrogenation of CO₂ is one of attractive routes to chemical synthesis from the point of not only the fossil resource saving but also the recycle use of emitted global warming gas and it is also interesting as a model reaction to the dark reaction in photosynthesis. Ethanol is one of important basic chemicals. It is easily converted to various chemicals such as ethylene, acetic acid, acetaldehyde, diethyl-ether and so on. From this point, we have been studying an effective synthesis of ethanol from H₂/CO₂ feedstock and developed several solid catalyst systems such as promoted Rh/SiO₂ catalysts [1], promoted Co/SiO₂ catalysts [2] and K/Cu-Zn-Fe mixed oxide catalysts [3]. However, ethanol selectivity of these catalysts is not enough. This is the reason why we have investigated the homogenous system presented here.

Catalytic hydrogenation of CO₂ was conducted using a batch reactor at a high-pressure condition. All chemicals used here were commercially available and used without any further purification. Products were analyzed by gas chromatography. Ru₃(CO)₁₂ was selected as a main catalyst after screening. Table 1 shows reaction results at various conditions. Ethanol selectivity was much improved up to 36.2% by the addition of Co₂(CO)₈ co-catalyst and the increase of reaction pressure up to 290 atm. Both an influence of reaction conditions and roles of co-catalyst and additives to the ethanol selectivity will be discussed as well as the reaction mechanism.

Table 1. Influence of reaction conditions on ethanol synthesis

Catalyst system (mmol)	Pressure (atm)	CO ₂ Conv. (%)	Product Selectivity (C-base %)			
			CH ₃ OH	C ₂ H ₅ OH	CO	CH ₄
Ru ₃ (CO) ₁₂ (0.19)-LiBr(11.2)	150	36.7	38.2	6.2	8.9	36.7
Ru ₃ (CO) ₁₂ (0.19) - Co ₂ (CO) ₈ (0.84)-LiBr(22.4)	150	32.9	46.5	16.1	23.6	13.8
Ru ₃ (CO) ₁₂ (0.19) - Co ₂ (CO) ₈ (0.84)-LiBr(22.4)	290	35.4	35.8	25.3	19.7	17.3
<u>Ru₃(CO)₁₂ (0.19) - Co₂(CO)₈ (0.84)-LiBr(44.8)</u>	<u>290</u>	<u>44.1</u>	<u>26.4</u>	36.2	<u>11.6</u>	<u>22.7</u>

Reaction Condition: H₂/CO=5/1, Temp.=200□, Solvent=Bu₃PO(14g), Reaction time=18 hr.

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Oral Presentation

Genes and proteins involved in carboxylation reactions from autotrophs with non-Calvin type CO₂ fixation pathway

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Hydrogenobacter thermophilus, a thermophilic hydrogen-oxidizing bacterium with a reductive TCA cycle (1), and *Acidianus brierleyi*, a thermophilic sulfur-oxidizing archaea with a modified 3-Hydroxypropionate cycle (2), were used in this study.

In terms of *Hydrogenobacter*, genes and proteins involved in Pyruvate: ferredoxin oxidoreductase (POR) and 2-Oxoglutarate: ferredoxin oxidoreductase (OGOR) were analyzed. POR has been shown to have 4 subunits (3). However, when *por* gene were isolated, it had additional *orf*, that had homology with ferredoxin, just upstream of the four genes (ferredoxin related gene [*porE*]-*porD-porA-porB-porG*). When *E. coli* with above five genes was cultivated, the cell extract had strong POR activity toward CO₂ evolution. In contrast to this, the cell extract from a transformant with four genes (*porD-porA-porB-porG*) had a very little POR activity toward CO₂ evolution. Analysis by active staining also showed that only the cell extract from a transformant with five genes gave positive bands. Interestingly, PORD, PORA, PORB, PORG, and PORE can be reconstituted after separate expression using *E. coli*. Analysis by using such system also showed that all five proteins are needed to show POR activity toward CO₂ evolution. OGOR has been shown to have two subunits (4). Cloning of the gene resulted in finding other two genes just downstream of *gorB* (*gorA-gorB-orf3-orf4*) (5) and another set of genes, which have homology with ferredoxin oxidoreductases (FOR), upstream of *gorA* in an opposite direction (*forD-forA-forB-forG-forE-forF*). At first, substrate specificity of FOR was analyzed by using a cell extract from a transformant with five genes (*forD-forA-forB-forG-forE*; *forE* has homology with ferredoxin). The extract showed only OGOR activity when various 2-oxo acids (2-oxoglutarate, 2-oxobutyrate, 2-oxoisocaproate, 2-oxoisovalerate, oxalacetate, oxomalonate, pyruvate, phosphoenolpyruvate) were used as substrates. This result shows that FOR codes another OGOR. In the next step, for each set of genes (*gor* and *for*), various transformants were prepared to clarify the genes necessary for the OGOR reaction toward CO₂ evolution. As for *gor*, *gorA* and *gorB* were sufficient to show the activity. As for *for*, *forD-forA-forB-forG-forE* was needed to show the activity; cell extract from a transformant with *forD-forA-forB-forG* had essentially no activity. Attempts to demonstrate carboxylation reactions by recombinant proteins (POR, OGOR, and FOR) are now under way.

In terms of *Acidianus*, Acetyl-CoA carboxylase was purified by using columns of Streptavidin and Gel-filtration from the cell extract of *Acidianus* grown autotrophically. The specific activity of the purified enzyme toward Acetyl-CoA was 14.51 U/mg; interestingly, the purified enzyme also had propionyl-CoA carboxylase activity (11.96 U/mg), which implies that only one enzyme catalyzes the two carboxylation reactions of 3-Hydroxypropionate cycle in *Acidianus*. From SDS-PAGE analysis, the purified enzyme was shown to be composed of three subunits (Molecular mass; 62, 59 and 20 KDa). The molecular mass of the native protein was estimated by gel-filtration to be 530 KDa, which shows that the subunit structure is $\alpha_4\beta_4\gamma_4$. The cloning of the genes are now under way.

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Oral Presentation

CO₂ REFORMING OF CH₄/NATURAL GAS OVER SUPPORTED CATALYSTS ON THE BASE OF THE VIII GROUP METALS

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The reaction between carbon dioxide and methane causes a great interest as a prospective process for utilization of both green-house gases with synthesis-gas production. The industrial use of this process is limited by a low resistance of catalysts to coke formation.

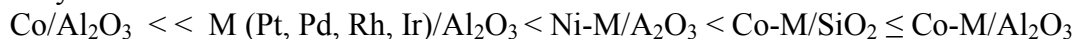
Recently we have reported that the modification of cobalt-containing catalysts supported on alumina by noble metals causes the increase of their activity and resistance to coke formation [1]. At moderate conditions ($\leq 600^\circ\text{C}$ and $P = 0.2\text{--}1.0\text{ MPa}$) both synthesis-gas and oxygenates are produced from carbon dioxide and methane by one step.

In this paper the interaction between carbon dioxide and methane over mono- and bimetallic (VIII Group metals: Co, Ni, Pd, Pt, Rh, Ir) supported on alumina and silica catalysts have been studied. Also CO₂ reforming of the natural gas over bimetallic Co-containing catalyst has been studied with the purpose of the future use of real gases.

The total metal content is 5 weight % and ratio Co/Ni : M = 1:1. In the case of Co-Pd catalyst the Pd content was varied from 2 to 50% (from total metal content). The process was carried out in a flow reactor under pressure 0.1 - 2.0 MPa and varying of experiment temperature from 200 to 1200°C and space velocity (S.V.) from 500 to 2000 hr⁻¹, ratio CO₂:CH₄ and CO₂:alkanes were constant 1:1, Ar content in an initial reacting mixture was 80 vol. %. The natural gas basically consists of propane-butane (40 and 50 vol. % accordingly).

Conversion degree of the initial reagents (CO₂, CH₄) depends on the catalyst nature and experiment conditions. On all catalysts the conversion of both reactants grows with increase of experiment temperature and decreases with pressure increase. All catalysts except Co/Al₂O₃ are very active at the atmospheric pressure. 100% conversion of methane on bimetallic and monometallic noble metal containing catalysts is observed at temperature region from 650- 850°C under atmospheric pressure. CO₂ conversion does not get 100% even at 1200°C and is varied from 90.0 to 97.5% with temperature growth from 700 to 1200°C ($P=0.1\text{ MPa}$).

The significant differences in catalytic properties are observed under pressure. Catalyst activity and stability increase in order:



Synthesis-gas is a main product at atmospheric pressure. Under pressure in addition oxygenates (20-30%), water and negligible amount of hydrocarbons are produced. In some cases oxygen is produced at the beginning of the process.

In the case of CO₂ reforming of natural gas basically the synthesis-gas and olefins are produced. It has been supposed that the oxidative dehydrogenation of alkanes by CO₂ participation is occurred.

By TEM analysis carried out after reaction it was observed the crystal coke on the monometallic Co-containing catalyst, amorphous carbon on the monometallic noble-containing catalysts and no carbon compounds on the bimetallic catalysts.

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Oral Presentation

PHOSPHOENOLPYRUVATE CARBOXYLASE: THREE DIMENSIONAL STRUCTURE, REACTION MECHANISM AND REGULATION

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Phosphoenolpyruvate carboxylase (PEPC, EC4.1.1.31) catalyzes the irreversible reaction of phosphoenolpyruvate with HCO_3^- to form oxaloacetate and P_i using Mg^{2+} as a cofactor. The enzyme is widespread in all plants and most bacteria, and performs anaplerotic functions by replenishing C4-dicarboxylic acids for the synthesis of various cellular constituents and for the maintenance of the citric acid cycle. About 30% of total fixed carbon depends on PEPC in cyanobacteria. Higher plants have several isoforms of PEPC with different physiological functions. In C4 and CAM plants, one of the PEPC isoforms is expressed abundantly and is involved in the photosynthesis by primarily capturing atmospheric CO_2 . Molecular structural studies on PEPC are thus expected to provide clues for the development of innovative strategies for the augmentation of productivity of photosynthetic organisms and for the conversion of CO_2 into useful organic compounds.

PEPCs are composed of four identical subunits with an M_r of 95-110 kDa. The primary structure was first deduced from a cloned DNA of *Escherichia coli* in 1984 by us. Since then, more than 25 molecular species of PEPC have been established including those from maize, a cyanobacterium and an extreme thermophile, which were studied by us.

[I] The 3D structure of PEPCs from *E. coli* and maize were determined at 2.8Å resolution (1). The four subunits are arranged in a "dimer of dimer" form. The contents of α -helices and β -strands are 65% and 5%, respectively. All of the 8 β -strands, which are widely dispersed in the primary structure, participate in the formation of a single β -barrel. Above C-terminal side of this barrel the catalytic site is located. There are two flexible glycine-rich loops (I and II) which plays important roles in catalytic activity. The primary structures of PEPCs from thermophiles, *Thermus* sp. and *Synechococcus vulcanus*, will also be presented and discussed their molecular strategies of thermostability.

[II] A possible 3-step reaction mechanism of PEPC will be discussed on the basis of 3D structural analysis and mutational studies, paying special attention to a conserved His-138 (*E. coli* PEPC) and loop II (702-708) (1, 2).

[III] PEPCs from higher plants are regulated by both allosteric effectors and reversible phosphorylation (3). They are feedback inhibited by L-aspartate or L-malate, and activated by sugar phosphate such as glucose 6-phosphate or fructose 1,6-bisphosphate. The site of regulatory phosphorylation is Ser near the N-terminus and is lacking in bacterial PEPC. The binding sites of these effectors and possible molecular mechanism of activation by phosphorylation will be presented. Possible usefulness of a mutant enzyme desensitized to feedback inhibition (K620S) will be discussed.

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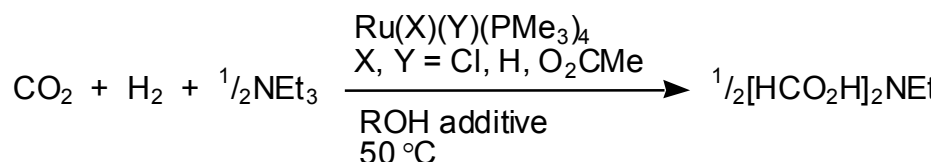
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Oral Presentation
**RECENT DEVELOPMENTS IN THE HYDROGENATION OF CO₂ CATALYZED BY
 RUTHENIUM PHOSPHINE COMPLEXES**

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One of us reported, a few years ago, that homogeneously-catalyzed CO₂ hydrogenation to formic acid was faster if the CO₂ were in the supercritical state.¹⁻³ The reason for the high rate, at the time, was not known. After a hiatus of several years, we have recently reopened the investigation in order to pin down the reasons for the success and to study the kinetics, mechanism, catalyst, solvent effects and other aspects of the reaction.



While the investigation has only just started, we are pleased to report that we have identified the reason for the high rate.⁴ We have also found that, although methanol was used as an additive in the earlier study, a far higher rate of reaction can be obtained if the additive is an alcohol sufficiently acidic to protonate the amine; a 1 h reaction in the presence of pentafluorophenol (C₆F₅OH) yields more formic acid than a 10 h reaction in the presence of MeOH, all other factors being equal.⁵

We have also tested 25 amines and other bases for effectiveness in the reaction; only 3 were highly effective. A wide range of phosphines and ligands were tested after a new and highly tunable family of in-situ catalysts for CO₂ hydrogenation was developed.⁶ The results will be interpreted in terms of the possible mechanisms.

Finally, we found that the hydrogenation of CO₂ in CHF₃-expanded methanol is faster, and in ethane-expanded methanol is slower than that in normal liquid methanol.^{4,7}

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Oral Presentation
A Highly Effective Catalyst for CO₂ Reforming of Methane:
Ni/Ce-ZrO₂/θ-Al₂O₃

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As a method for CO₂ utilization, CO₂ reforming of methane has received increasing attention.^{1,2} In our previous studies, we performed the CO₂ reforming of methane over Ni/ZrO₂ catalysts.³ In the next step, the zirconia supports were modified with Ce in order to improve the oxygen storage capacity of the catalysts.⁴ In this work, Ni/Ce-ZrO₂/θ-Al₂O₃ was prepared as a more practical type of catalyst and examined together with Ni/γ-Al₂O₃ and Ni/θ-Al₂O₃ in the reaction.

The Ni/γ-Al₂O₃, Ni/θ-Al₂O₃ and Ni/Ce-ZrO₂/θ-Al₂O₃ catalysts with 3% Ni loading were prepared by the impregnation method. Prior to catalytic activity test, the catalysts packed in the reactor were reduced *in-situ* with 5% H₂/N₂ at 700 °C for 2 h. Then the reactor was purged with nitrogen while being heated to the reaction temperature. The reactant gas mixture was composed of CH₄:CO₂:N₂ = 1:1:3. TPR experiments were carried out in conventional apparatus using 5% H₂/H₂ gas with a heating rate of 10 °C/min.

The activities of the catalysts were compared with one another at 800 °C and 60,000 cc/g_{cat}·h. The results clearly show that Ni/Ce-ZrO₂/θ-Al₂O₃ catalyst is highly active and stable in CO₂ reforming of methane. Both Ni/γ-Al₂O₃ and Ni/θ-Al₂O₃ showed high initial activity, but the activities declined slowly and steadily with time on stream due to the phase transformation with the difference of the slope. However, in the case of Ni/Ce-ZrO₂/θ-Al₂O₃ catalyst, CH₄ conversion was almost unchanged with time on stream. Thus, it is confirmed that Ce-ZrO₂ pre-coating makes beneficial effect on both the activity and the stability. This result can be explained as follows. Ce-ZrO₂ pre-coating inhibits phase transformation of θ-Al₂O₃ into α-Al₂O₃, enhances oxygen storage capacity, prevents carbon formation resulting from the strong interaction between Ni and Ce-ZrO₂ pre-coated θ-Al₂O₃.

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Oral Presentation
Synthesis of Catalysts for Conversion of CO and CO₂ to Methanol

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ABSTRACT

Catalysts containing copper, zinc and aluminum oxides are widely used in chemical industry, particularly in methanol synthesis process. In the present study, the effect of pertinent preparation parameters on catalysts' activity has been studied, applying the saturated fractional factorial experimental design method. The influence of time and temperature of calcination, aging time, method of mixing of reactants solutions, the nature of the precipitant and the molar ratio of the latter to metal nitrates have been investigated. The catalysts prepared, using sodium carbonate showed higher activities relative to those synthesized by applying sodium hydrogen carbonate. Higher temperatures and longer time of calcination have profound effects on the activity of catalysts prepared, using sodium hydrogen carbonate. Shorter aging times and higher molar ratios of precipitant to metal nitrates promoted the activity of catalysts prepared by sodium carbonate. In case of using sodium hydrogen carbonate as the precipitant, the aging time should be maintained as short as possible in order the catalysts to acquire higher activities. The activities of catalysts have been determined using a fixed bed catalytic reactor. The reactants' feed consisted of hydrogen gas with partial pressure of 2.78-13.03 bar, carbon monoxide with partial pressure of 0.052-2.21 bar and carbon dioxide with partial pressure of 0.0-0.684 bar. The operating temperature was 210-270°C. The catalyst with the highest activity was prepared using sodium carbonate as the precipitant. The aging time was 37 minutes and calcination temperature was 350°C. Some physical characteristics of the latter were as follows,

BET (m ² /g)	Copper surface area (m ² /g)	Density (g/cm ³)
27.98	21.91	4.14

The activity of this catalyst was found to be 5.2 (millimole methanol)/(h)(g catalyst). Such an activity is higher than that of a number of commercial catalysts.

Poster Presentation

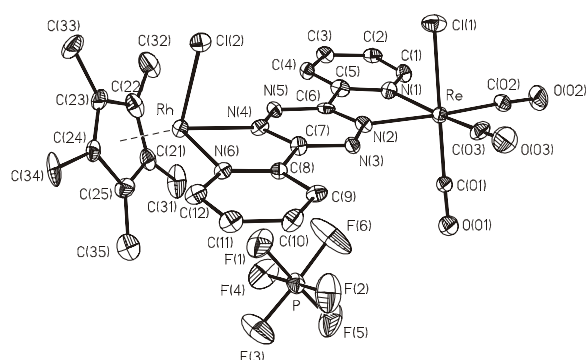
Primary Activation Processes of Heterodinuclear Complex Ions $[(\eta^5\text{-C}_5\text{Me}_5)\text{ClM}(\eta\text{-L})\text{Re}(\text{CO})_3\text{Cl}]^+$, $\text{M} = \text{Rh}$ or Ir , for the Reductive CO_2/H^+ Conversion

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Heterodinuclear complexes with two different functional metal centers are attractive molecular versions of bimetallic catalysts. The molecule(L)-bridged precursor complexes $[(\eta^5\text{-C}_5\text{Me}_5)\text{ClM}(\mu\text{-L})\text{Re}(\text{CO})_3\text{Cl}]^+$ contain two coupled organometallic reaction centers of which the rhodium or iridium sites M are capable of hydride transfer catalysis whereas the rhenium centers have a potential for CO_2 conversion. Each of the sites requires activation through reductive elimination of metal-bound chloride. The mechanisms of the primary reductive activation processes and the interaction with the substrates CO_2 and H^+ were investigated through a combination of electrochemical and spectroscopic techniques (IR, UV-vis, EPR) for a series of complexes with symmetrically bridging bis-chelate ligands $\text{L} = 2,2'$ -bipyrimidine, $2,2'$ -azobispyridine, $2,5$ -bis(1-phenyliminoethyl)pyrazine or $3,6$ -bis(2-pyridyl)-1,2,4,5-tetrazine (bptz).



Poster Presentation

Direct Urethane Synthesis by the Reaction of Aminoalcohol with Carbon Dioxide under Supercritical Conditions

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From the standpoint of the protection of environment, the synthesis of urethane derivatives with carbon dioxide has much attention as utilizing carbon dioxide, which is a safe and cheap C1 source for organic compounds. Cyclic urethane synthesis from 2-amino-1-alkanols and carbon dioxide is also attractive method, but little study has been succeeded, and few successful methods need equimolar halo-compounds, such as trichloroethane, tetrachloromethane and chloroform.[†] We have attempted the reaction of 2-amino-1-alkanols with carbon dioxide under supercritical carbon dioxide,[‡] and we have found that urethane synthesis is successfully proceeded in high (or quantitative) yields under scCO₂ within 1 hour (to few minutes) from 2-amino-1-alkanols in the presence of DCC as dehydrolysis reagent. Pressure effects are also examined, and the urethane yields and intermediate yields of this reaction are increased with increasing pressure. From our results, we achieved the non-halogen reaction system of urethane synthesis under scCO₂, and this reaction is much faster than previous reaction of cyclic urethane synthesis.

[†] Cyclic urethane synthesis is also achieved by the reaction of aminoalcohol with other reagents, such as carbon monoxide, diethyl carbonate, etc., but no carbon dioxide is need in these reactions. [‡] Reaction temp. is 40°C

Oral Presentation
High-Pressure NMR Studies in Supercritical Media

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Supercritical fluids are potentially ideal media for conducting catalytic reactions that involve gaseous reactants, including H₂, CO, and CO₂. The presence of a single homogeneous reaction phase eliminates the gas-liquid mixing problem of alternative two-phase systems, which can limit process rates and adversely affect product selectivities. Our research employs a high-pressure NMR probe with a high-sensitivity toroid detector to provide *in situ* spectroscopic analysis of catalytic reaction intermediates. Emphasis has been placed on the cobalt carbonyl catalyzed hydroformylation of olefins to aldehydes which is referred to as the oxo process. The oxo process is one of the largest industrial scale catalytic processes. Our work has shown that the reaction proceeds cleanly in supercritical carbon dioxide with improved product selectivity for the desired linear aldehyde. In addition, the *in situ* NMR results definitively establish that •Co(CO)₄ radical is present at mechanistically significant concentration levels under standard oxo reaction conditions. This highly reactive odd-electron organometallic complex promotes facile hydrogen atom transfer reactions. The activation parameters for hydrogen atom transfer between cobalt and manganese metal centers have been measured. Additional parameters measured for the oxo process in supercritical CO₂ include (1) the steady-state concentrations of the catalytic intermediates, (2) the thermodynamics and forward and reverse rate constants for the hydrogenation of Co₂(CO)₈, and, (3) the net rate and product selectivity for the overall hydroformylation reaction. Comparisons between the standard oxo and the phosphine modified or Shell process will be made.

More recent work is directed toward exploring the properties of a new type of reaction medium formed by dispersing reverse micelles with high-density aqueous cores in a low-density supercritical fluid as the continuous phase. This unique combination of properties should facilitate catalytic reactions by facilitating mass transfer over more traditional reverse micellar systems that employ more viscous organic solvents for the continuous phase. Importantly, the size of the micellar reaction core is readily tuned on the nano scale by controlling the water to surfactant ratio. Micellar systems of this nature hold significant promise for the controlled synthesis of nano particles and catalysts.

Oral Presentation

Managing the Global Carbon Cycle

Klaus S. Lackner
Columbia University
May 2001

As human activities begin to dominate the natural carbon cycle, the continued use of fossil carbon in the energy sector will require deliberate management of the entire cycle. Rather than just considering the impact of carbon dioxide emissions on the atmosphere, one will have to consider the tightly coupled reservoirs that make up the surface carbon pool, i.e., the atmosphere, the ocean, terrestrial biomass, and terrestrial soil. This perspective actually simplifies the debate in that it gets away from the details of climate modeling and brings the task of carbon management into sharper focus.

Compared to the size of natural carbon fluxes entering and leaving the combined surface pool, anthropogenic carbon fluxes, mainly resulting from the combustion of fossil fuels, are already very large. In addition, the amount of excess carbon that has been introduced, and is likely to be introduced in the foreseeable future, is large compared to the natural uptake capacity of these reservoirs. One century of present carbon consumption (600 Gt) would equal the entire biomass carbon, all the carbon in the atmosphere, more than a third of all soil carbon, or half of the carbon that as bicarbonate would lower the ocean pH everywhere by 0.3. However, historic rates of world economic growth suggest that the next century's carbon consumption could be larger than the constant rate projection by a factor of three to five. The resulting influx of fossil carbon into the surface pool would make it virtually impossible to manage the carbon cycle just by modifying natural fluxes among the reservoirs of the surface pool.

Fossil fuel resources could sustain current demand for at least ten to twenty centuries. Reliance on resource limitations will not solve the problem. Ignoring the problem would probably cause profound environmental and ecological changes more serious than those due to climate change. Managing the natural and man-made carbon cycle can no longer be avoided.

Strategies for managing the carbon cycle range from short-term adjustments in carbon fluxes to ameliorate the immediate build-up of carbon dioxide in the atmosphere to the engineering of permanent carbon sinks outside of the surface pool that could accept all of the fossil carbon. Improvements in energy efficiency and increased use of renewable energy will provide welcome support in reducing excess carbon fluxes, but by themselves they are not likely to solve the problem. For the foreseeable future, worldwide reductions in the use of fossil carbon are not desirable, as they would severely hamper the necessary economic growth in the developing nations.

We will explore for how long and at what level fossil fuel use could be sustained. Without carbon dioxide disposal, fossil fuels are not sustainable even on a time scale as short as decades, but technologies for eliminating all emissions from fossil fuels including carbon dioxide are under development and are likely to succeed. With carbon dioxide disposal, fossil fuel use is sustainable far longer.

Oral Presentation
Catalytic CO₂/HCO₃⁻ reduction in aqueous solutions

Laurenczy, G.¹, Joó, F.² and Nádasdi L.^{1,2}

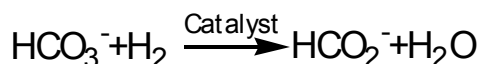
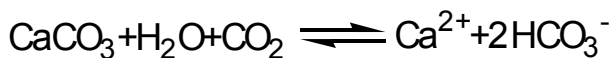
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The huge amount of CO₂, present in the atmosphere, hydrosphere and emitted as waste from the combustion of fossil raw materials, suggests that it could be an interesting basic C1-unit in a future carbon based synthetic chemistry. The same applies for carbonate rocks, dolomite and limestone. Although numerous chemical, technical, and economic questions have to be solved beforehand - such as the production of the hydrogen needed, product separation, catalyst recuperation - this is a great challenge for chemists, given that the most important reaction in volume on the Earth is photosynthetic carbon dioxide reduction.

Several attempts have been made to reduce CO₂: in the presence of amines, platinum group metal complexes have been found active to produce formic acid, formate esters or formamides (in organic phase, in biphasic systems or in supercritical CO₂).

In this contribution we present our results on the reduction of aqueous carbon dioxide/limestone/dolomite systems using water soluble Rh- and Ru-phosphine catalysts. For these reactions we do not use any amine as a thermodynamic sink for the reduction.



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Topic: CO₂ Hydrogenation

Presentation preference: oral

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Oral Presentation

Transport of micelles and monomeric solutes in supercritical CO₂

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Water-in-CO₂ microemulsions have been utilized in a wide range of applications, including separations, enzymatic reactions, and catalytic reactions between polar and nonpolar molecules. Applications of water-in-CO₂ microemulsions prompt a need for measurement tools that support fundamental investigations of the dynamics and transport in such media. Towards this end, we have used electrochemical techniques to study the transport of small molecules and micelles in water-in-CO₂ microemulsions. By controlling the partitioning of electroactive probes based on their solubility, we have determined the diffusion coefficients of ferrocene (Fc) in the CO₂ phase and of the micelle in water-in-CO₂ microemulsions. Investigations of the dependence of the diffusion coefficients of charged species on the volume fraction of the micelles show some kind of attractive interactions between micelles, which in turn increase the viscosity of microemulsions. In contrast, the diffusion coefficient of Fc is independent of the volume fraction change, which allows the determination of the viscosity of pure CO₂.

Oral Presentation
CATALYTIC HYDROGENATION OF CO₂ AND CO₂
RICH BIOSYNGAS TO CLEAN FUELS

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In last decade Carbon Dioxide has received a great attention because it is cleared that CO₂ is the most effective global warming gas showing the anthropogenic distribution to global warming is more 64% and an enormous amount of more 7.4 billion tons is emitting into the atmosphere annually. There are many reports ^{1,2)} which indicates the concentration of CO₂ will rise to 750 ppm in 2100 if we don't do any works for the sequestration, mitigation and utilization of CO₂.

The products in the sense of mass consumption of CO₂ into renewable clean energy and valuable chemicals are hydrocarbons and methanol. To get the hydrocarbons/wax from synthesis gas, the Fischer-Tropsch reaction is well known since 1940s. However a few papers have published on the hydrogenation of CO₂ to hydrocarbons.

Recently the biomass has received a great attraction as a sustainable and renewable clean energy source because it is carbon neutral and contains very low sulfur and nitrogen than crude oil. ³⁾

In this paper, the authors will introduce the approaches and results of other authors and mainly ours. The authors had screened some catalysts. Among them, Fe/Cu based catalyst showed the activity more than 2,000 hrs. We have changed the promoters and supports and found that alumina as a support is prominent for the reaction of CO₂ and CO₂ rich biosyngas.

The reactions were carried out mainly in a fixed bed reactor and in a slurry bed reactor. The different results from both reactions are explained. In a slurry bed reaction, the formed water on the catalyst surface may affect the inferior reactivity comparing to fixed bed reaction. ⁴⁾

The reasons of deactivation of impregnated Fe-K catalyst and co-precipitated catalyst were elucidated by means of BET, XRD, XPS, Moessbauer, TPR, TPDC and Chemisorptions. The former caused by deposition of carbonaceous material on the catalyst and the latter by the crystal growing and change of metal composition of the catalyst. ^{5,6)}

To accumulate the engineering data, the authors operated bench scale system which equipped with recycle and reforming units. The products are separated from each fraction and quantified and identified the structure. The material balance is made. On the base of these data, a trial economic evaluation of the CO₂ hydrogenation process was attempted. The kinetic study also was performed. ⁷⁾ The similar reactions in fixed and slurry bed reactions of CO₂ rich biosyngas were tested. From the results, it is proposed a two step reaction with combination of methane reforming and one through reaction for the CO₂ separation.

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Poster Presentation
**Lewis Base Adducts of Zinc Complexes for the
Coupling of CO₂ and Epoxides**

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Utilization of CO₂ as a C₁ feedstock has seen widespread growth in recent years, largely due to an increasing concern over the rapid depletion of natural resources. Of particular interest is the use of CO₂ in the formation of polycarbonates from oxiranes. Inoue discovered this reaction in 1969, using a heterogeneous zinc based catalyst.¹ Our group has been active in this area for many years developing homogenous catalysts for the copolymerization of CO₂ and epoxides.² Due to the work of Kim *et al.*,³ we have begun work using simple zinc halides with functionalized pyridine ligands coordinatively bound to zinc as catalysts for the copolymerization reaction of CO₂ and epoxides.

We have synthesized a variety of zinc catalysts with the halides Cl, Br, I and pyridine ligands ranging from 3-trifluoromethylpyridine to 2,6-dimethoxypyridine, which form four-coordinate tetrahedral catalysts. The ZnBr₂(2,6-dimethoxypyridine)₂ catalyst performs the coupling reaction of CO₂ and cyclohexene oxide best displaying turnover frequencies of 34.6 g poly./g Zn·hr with ~85% carbonate linkages as determined by ¹H NMR spectroscopy. *In situ* infra-red studies have been performed utilizing a high temperature, high pressure ReactIR[®] probe (Figs. 1-3) to gain mechanistic insight into this system under polymerization conditions. Our initial kinetic studies show this system to be first order in monomer as well as first order in catalyst. Further details and results will be discussed.



Figure 1 High temperature, high pressure ReactIR[®] probe

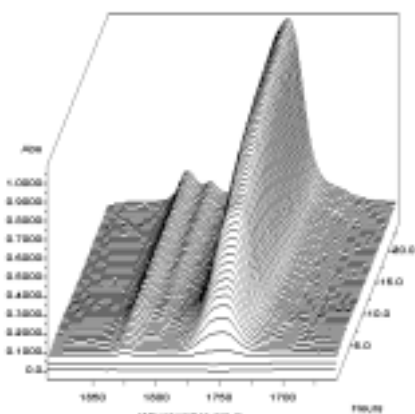


Figure 2 *In situ* IR monitoring of the copolymerization reaction (90°C, 55 bar)

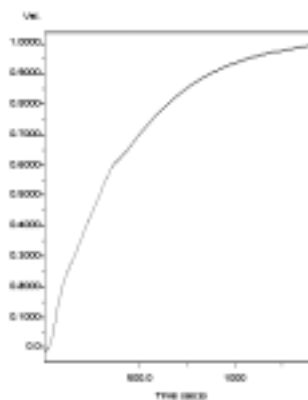


Figure 3 Trace of the absorbance at 1750 cm⁻¹

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Oral Presentation
Microbiol CO₂ Fixation: An Overview

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Most people associate autotrophic CO₂ fixation with the photosynthetic carbon cycle or Calvin cycle, which key enzyme is ribulose - 1,5 - biphosphate carboxylase/oxygenase or RuBisCo. Via this pathway about 150×10^9 tons of CO₂ is fixed per year and reduced by water with liberation of O₂ to cell material and lignocellulosic biomass. About 80% of the biomass is in aerobic environments recycled to form CO₂ and H₂O. In anaerobic environments about 20% of the biomass is fermented to mostly lactate, ethanol, acetate, CO₂ and H₂. Very little of the H₂ escapes into the atmosphere, instead it is assimilated by microorganisms and used for the reduction of CO₂ and other oxides. Methanogenic and acetogenic bacteria are the two major groups which fixes CO₂ with H₂ as reductant to form methane and acetate, respectively. They grow autotrophically, and all cell carbon comes from CO₂. Instead of the Calvin cycle these bacteria use the acetyl-CoA pathway or modification of it, the reductive citric acid cycle, and the glycine synthase pathway. These pathways and properties of their key enzymes will be discussed.

Oral Presentation
**Enhancing CO₂ Utilization and Potential Sequestration in Temperate Climates
with C4 Photosynthesis: Theoretical Analysis and Practical Experience with
Miscanthus.**

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In maximizing the CO₂ uptake by plants, C4 photosynthesis offers theoretical advantages over C3 photosynthesis. Yet in practice, C3 plants are often more efficient in the temperate zone. By minimizing photorespiration, C4 plants have higher potential efficiencies of radiation, nitrogen and water use. In cool climates, photoinhibition and impaired development of the photosynthetic apparatus have limited the value of C4 photosynthesis. A mean temperature of 26°C was suggested as the threshold above which photosynthesis in C4 photosynthesis is superior. As a result the potential superiority of C4 photosynthesis can currently only be realized for a short part of the year in much of the USA. An analysis will be presented which shows, from biochemical theory, that C4 photosynthesis has the potential to attain superior rates of photosynthesis relative to C3 even at 10°C, if low temperature damage of the development of the photosynthetic apparatus is prevented. Our recent studies of the C4 grass *Miscanthus x giganteus* appear to validate this theory.

In the last few years, several C4 species have been identified with good cold temperature tolerance. Among these, *Miscanthus x giganteus* appears exceptional. The parents of this hybrid are found at high altitude in Japan, and may have evolved low temperature tolerance on these altitudinal gradients. Extensive trials in W. Europe show that leaves of *M. x giganteus* develop about a month ahead of corn without any significant low temperature impairment of photosynthetic capacity. Early growth in the spring and survival of the leaf canopy into the late Fall, result in this genotype being twice as efficient, by comparison to corn, in intercepting radiation and similarly more efficient in using the intercepted radiation to assimilate CO₂. Its efficiencies of radiation, nitrogen and water use at 52°N were as high as those reported for C4 species in tropical and sub-tropical climates.

M. x giganteus has other properties that make it of potential value for CO₂ utilization and sequestration. It is a rhizomatous perennial that produces an annual crop of bamboo like stems, harvested in the late fall or winter. In Europe these stems are being used for co-firing power generation plants, and also being considered as feedstock for biobased industries. In E. England, over a period of 3 years, rhizome and root deposition in the soil represented an estimated 15 t (CO₂) ha⁻¹ y⁻¹. Shoot production represented a further 30 t (CO₂) ha⁻¹ y⁻¹. Models, based on the European trials, suggest that similar rates of CO₂ uptake could be achieved in much of the northern half of the US with this genotype.

Finally, *M. x giganteus* demonstrates that C4 photosynthesis can function at much lower temperatures than previously thought possible. Comparisons with other C4 species at the physiological, biochemical and molecular levels are revealing how low temperature adaptation has been achieved, and how other C4 species might be engineered to extend the temperature range over which they can efficiently utilize CO₂.

Oral Presentation

Evaluation of Wind Energy Utilizing Methanol System

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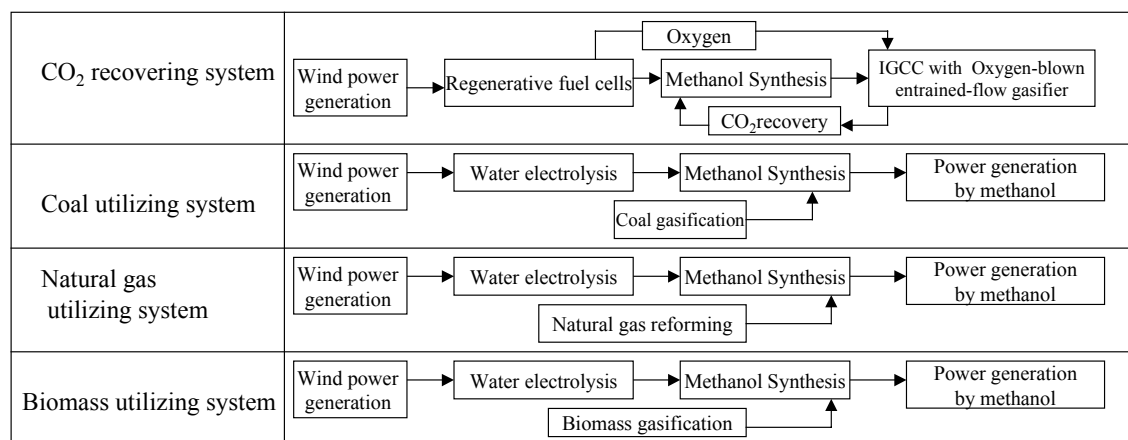
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Introduction

In order to solve global warming induced by enormous amounts of carbon dioxide emission, RITE has developed 'CO₂ global recycling system' which converts renewable energy into liquid fuel such as methanol, synthesized by catalytic hydrogenation of separated and recovered CO₂. As a result, this system was presumed to be viable in the future, with the establishment of "Carbon tax" and by using hydraulic power generation as a renewable energy. However, for practical application of this renewable energy transporting system by methanol synthesis, it is necessary to evaluate not only about separated and recovered CO₂ but other carbon sources and renewable energy.

In this study, we proposed and evaluated renewable energy transporting systems which synthesize methanol from wind power generation, at the viewpoints of energy efficiency, methanol cost, CO₂ reduction rate, etc. Moreover, we evaluated the feasibility of proposed wind energy utilizing systems by comparing it with current fossil fuel systems, and also with similar systems utilizing hydraulic power generation. The data of wind and geographical conditions were collected, considering that the wind power generation plant will be installed at the eastern coast of Russia. The evaluated systems are



shown in figure below.

Fig. Concept of Proposed Wind Energy Utilizing Systems

Results and Discussion

Biomass utilizing system showed the sufficient CO₂ reducing effect within proposed systems from the evaluation of CO₂ reduction rate and CO₂ reducing cost. This cost was much lower than the current CO₂ reducing cost, therefore this system is considered feasible for CO₂ reduction assuming the decrease of wind power generation price.

This work was supported by the New Energy and Industrial Technology Development Organization (NEDO).

Poster Presentation

Kinetic study of catalytic CO₂ hydration by water-soluble model compound of carbonic anhydrase and anion inhibition effect on CO₂ hydration

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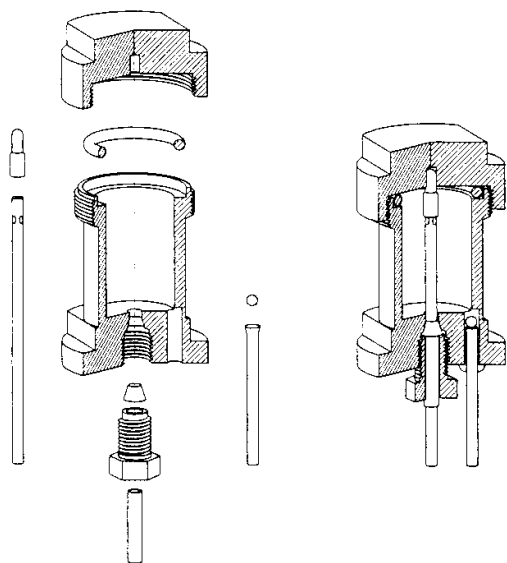
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A kinetic study of CO₂ hydration was carried out using the water-soluble zinc model complex for the active site of carbonic anhydrase [L1SZn(OH₂)], where **L1S** is nitrilotris(2-benzimidazolylmethyl-6-sulfonate), in the presence and absence of anion inhibitors NCS⁻ and Cl⁻. The obtained rate constants k_{cat} for CO₂ hydration were 5.9×10^2 , 1.7×10^3 , and $3.1 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ at 5, 10, and 15°C, respectively : the extrapolated ca. $10^4 \text{ M}^{-1} \text{ s}^{-1}$ at 25°C has been the largest among the k_{cat} s obtained using model complexes for carbonic anhydrase. It was also revealed that NCS⁻, Cl⁻ and acetazolamide play a role as inhibitor, since $k_{\text{cat}} = 7 \times 10^2$ and $2 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ for NCS⁻ and Cl⁻ at 15°C, respectively. The sequence of their magnitudes in k_{cat} is Cl⁻ > acetazolamide > NCS⁻, where the sequence Cl⁻ > NCS⁻ is confirmed for native carbonic anhydrase. The difference of k_{cat} or k_{obs} between NCS⁻ and Cl⁻ was resulted from the different stability constants 2×10^3 and $1 \times 10^2 \text{ M}^{-1}$ of [L1SZnNCS]²⁻ and [L1SZnCl]²⁻. The structures of inhibitor-binding zinc model complexes { [L1Zn(OH₂)]_{0.5} [L1ZnCl]_{0.5} }^{1.5+} (**1**_{0.5}**2**_{0.5}), [L1ZnCl]⁺ (**2**), and [L1ZnNCS]⁺ (**3**), where L1 is tris(2-benzimidazolylmethyl)amine, were determined by X-ray crystallography. The geometries around Zn²⁺ in **1**, **2** and **3** were tetrahedrally coordinated by three N atoms of benzimidazolyl group and one O atom of H₂O, Cl⁻ or N atom of NCS⁻.

Poster Presentation

***In situ* NMR Studies and Diffusion Imaging in Supercritical CO₂**

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Utilization of supercritical media for chemical reactions has increased considerably during recent years because of its attractive properties. Especially supercritical carbon dioxide (scCO₂) has gained in importance for it is nontoxic, easy to recycle and separate from other reaction components. In addition, it exhibits a low viscosity, a high diffusivity, and is fully miscible with reactive gases. Accordingly, scCO₂ has been used as the solvent for a variety of chemical processes and reactions such as polymerization, hydrogenation, hydroformylation, separation, and extraction. Many phenomena of scCO₂ such as the solute-solvent interactions and the diffusivity, which are well-known and understood in liquid media, are not sufficiently investigated in the supercritical state. With the toroid cavity autoclave (TCA, see Figure), i.e., a toroid NMR resonator that simultaneously functions as a pressure vessel for high-pressure and elevated-temperature studies, we have developed an *in situ* NMR probe design that is particularly suited for investigations of chemical reactions and for diffusion studies in supercritical fluids. The TCA allows for *in situ* studies up to 200 °C and, simultaneously, up to 400 bar. In addition, temperature and pressure are controlled and adjusted, if necessary, in the course of an experiment, and reactive components can be added with the TCA already pressurized. In this contribution, we present the results of *in situ* NMR studies that show several aspects of expected and unexpected behavior of diffusion and catalysis in scCO₂.

Oral Presentation
**PHOTOCATALYTIC REDUCTION OF CARBON DIOXIDE
BY GOETHITE UNDER SUNLIGHT IRRADIATION**

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The greenhouse effect by carbon dioxide is one of the worldwide problems. Therefore the technologies of the removal and conversion of carbon dioxide have been needed to establish. Some of these technologies have been industrialized. However the systems have needed high temperature and/or high pressure, that is, high energy for the removal and conversion, Most of the researches for the carbon dioxide reduction under mild experimental conditions have just started recently.

This report presents the photocatalytic reduction of carbon dioxide by goethite, which is immersed in aqueous solution, under sunlight irradiation at ambient temperature and atmospheric pressure.

Goethite sands with CO₂-saturated water in a glass vessel were illuminated by sunlight (> 50000 lux). Gas products of the photocatalytic reactions were analyzed by gas chromatography rising highly purity helium gas as carrier gas.

The carbon dioxide art goethite was reduced to carbon monoxide, methane, ethylene and ethane. Tile formation amounts of these compounds were 2.0×10^{-3} ml/g, 2.2×10^{-3} ml/g, 1.6×10^{-4} ml/g, and 9.0×10^{-4} ml/g for 10 h illumination, respectively. Furthermore, 7.6×10^{-3} ml/g of hydrogen was generated on goethite for 10 h sunlight illumination.

Poster Presentation

CO₂ Hydrogenation to Methanol and Ethanol over Highly Dispersed Co/SiO₂ Catalysts Derived from Acetate

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Highly dispersed 5wt%-Co(A)/SiO₂ catalysts were prepared by impregnating SiO₂ with an aqueous solution of cobalt acetate, and used as a catalyst for CO₂ hydrogenation at reaction conditions of $T = 473\text{--}508\text{ K}$, $P = 2.1\text{ MPa}$, $\text{H}_2/\text{CO}_2 = 3/1$ and $GHSV = 2000/\text{h}$. The Co(A)/SiO₂ catalyst without additives showed lower activity than the conventional Co(N)/SiO₂ catalyst derived from cobalt nitrate, of which Co crystallite size was estimated at 6 nm by XRD line broadening. However, methanol selectivity was much higher over the former catalyst than the latter, probably because of the high dispersion. The results of XPS, TPR and H₂ chemisorption suggest that the low activity is ascribed to the hardly reducible Co on the surface of Co(A)/SiO₂ catalyst. When a small amount of noble metal carbonyl, such as Ir₄(CO)₁₂ or Ru₃(CO)₁₂, was added to Co(A)/SiO₂ by the vapor phase deposition method, CO₂ conversion was drastically improved, and a trace amount of ethanol was formed, as well as methanol. Since Ir/SiO₂ did not show any activity for CO₂ hydrogenation, synergetic effect between Ir and Co(A)/SiO₂ was postulated. The XPS and TPR results indicate that Co²⁺ on the surface was readily reduced to highly dispersed metallic Co, probably with enlisting the spilt-over hydrogen on Ir of the Ir/Co(A)/SiO₂ catalyst. The Ir amount more than Ir/Co = 0.06 was sufficient for the promotion effect. When alkaline earth metal salts, such as Mg-, Ca- and Sr-acetates, were added to the Ir/Co(A)/SiO₂ catalyst, methanol selectivity was increased up to about 35% with suppressing CH₄ formation. On the other hand, ethanol selectivity was increased, when alkali metal (M^a) salts, such as Na-, K- and Cs-acetates, were added instead. A good correlation between the selectivity and basicity of M^a was observed, and ethanol selectivity was increased and conversion was decreased with the added amount. Consequently, the highest space time yield of ethanol up to 5.3 g/l/h was obtained over Ir/Co(A)-Na/SiO₂ catalysts at $T = 493\text{ K}$.

Table Reaction Results at T = 493 K

Catalyst*	CO ₂ conv.	CH ₄ selec.	CO selec.	MeOH selec.	EtOH selec.
Co(N)/SiO ₂	9.2 %	93.8 %	0.0 %	2.7 %	0.1 %
Co(A)/SiO ₂	0.5	15.0	67.0	17.1	0.0
Ir/SiO ₂	0.5	9.4	90.1	0.0	0.0
Ir/Co(A)/SiO ₂	10.0	68.2	9.6	20.3	0.4
Ir/Co(A)-Ca/SiO ₂	5.4	21.9	41.0	35.2	1.1
Ir/Co(A)-Na/SiO ₂	7.6	35.7	38.5	7.8	7.9

* Ir/Co/M = 0.13/1.0/0.67 (in atomic ratio).

Oral Presentation
Dehydrogenation of Ethylbenzene with Carbon Dioxide:
Effect of CO₂ as Soft Oxidant

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For the mitigation of global warming due to carbon dioxide, catalytic conversion of CO₂ has been extensively studied for last decade. Most of studies on this field have been concentrated on the utilization of carbon dioxide as a carbon source through catalytic reduction processes with various kinds of reductants. However, utilization of CO₂ has been recently attracted considerable attention as an oxidant, a promoter and a reactant for the production of useful chemicals. It is expected that this approach may open the new technology for CO₂ utilization. We have also reported that carbon dioxide can play a role as the soft oxidant in the oxidative conversions of several hydrocarbons. Moreover, it was found that CO₂ can suppress the total oxidation in the oxidative coupling of methane and alkylaromatics together with the increase of selectivity and the low rate of coke formation.

In this work, oxidative dehydrogenation of ethylbenzene (EB) with carbon dioxide has been carried out over supported iron oxide and vanadium oxide catalysts. This process is commercially operated by a large excess of superheated steam as a diluent using potassium-promoted iron oxide catalysts. It was found that carbon dioxide plays a key role as soft oxidant for promoting the catalytic activity as well as selectivity to styrene. The enhancement of the dehydrogenation activity and the selectivity was certainly ascribed to the promotional effect to the oxidative process by excess carbon dioxide. It was confirmed that the utilization of CO₂ as the oxidant over these catalysts increases equilibrium conversion to styrene as compared to that of the dehydrogenation with steam. In addition, the energy consumption required for the EB dehydrogenation using carbon dioxide was estimated to be much lower than that for the currently operating process using steam. It was demonstrated that CO₂ affinity of surface and nanodispersion of active sites via matrix isolation through supporting with high surface area supports greatly influence the individual catalytic activity in EB dehydrogenation with CO₂.

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Oral Presentation
**CO₂ Hydrogenation over Cu-containing Hybrid Catalysts
for the Synthesis of Oxygenates**

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Abstract

Methanol synthesis from CO₂ hydrogenation could be improved through in-site conversion of methanol into dimethylether (DME). Cu-based catalysts for methanol synthesis and solid acid catalysts for methanol conversion can be combined to make hybrid catalysts. It was observed within the thermodynamic constraints that the yield of oxygenates (methanol + DME) was enhanced through hybrid catalytic process

Cu/ZnO/ZrO₂ and Cu/ZnO/Ga₂O₃ were chosen as methanol synthesis catalysts and NaZSM-5, HZSM-5, H-Ga-silicates and SAPO-34 as acid catalysts for methanol conversion.

The hybrid catalysts of Cu/ZnO/ZrO₂ and H-Ga-silicate showed the highest yield of oxygenates. The modification of reducibility or oxygen coverage due to the interactions between methanol synthesis catalyst and zeolite was believed to affect the ability of oxygenates synthesis.

Poster Presentation

Electrochemical Separation of CO₂ Mixtures

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This poster will present the development and demonstration of a system that can pump CO₂ from low to high pressures using an electrochemically modulated carrier molecule. Traditional CO₂ separation techniques such as cryogenic distillation, adsorption, and membrane separation require about 20 times the theoretical minimum amount of energy required. The electrochemical process, however, approaches the thermodynamic minimum energy required for separation because phase changes, compression costs, and thermal processes are not required. In the application presented, an electrochemically modulated carrier absorbs CO₂ in its CO₂-philic oxidation state, and desorbs CO₂ in its non-binding state. Both modeling and experimental results will be presented.

The electrochemistry and CO₂ equilibria are critical in the function of this process. 2,6-di-tert-butyl benzoquinone was used as the redox active carrier molecule in this demonstration. A suitable solvent must also be chosen with redox potentials outside the range of that required by the carrier molecule. The solvent should also have a small CO₂ solubility to facilitate near complete desorption of CO₂ during the release phase. Room temperature ionic liquids (RTIL) provide an excellent solvent for this system, since RTILs are excellent ionic conductors, have low CO₂ solubility, and have a negligible vapor pressure, which eliminates the need to replenish evaporated solvent or remove solvent vapors from the treated gas stream. In this demonstration, the RTIL butyl-methyl-imidazolium hexafluorophosphate was used.

We designed and built a gas tight electrochemical cell in which a feed stream containing a low concentration of CO₂ in N₂ could be bubbled through a reduced quinone solution to load the solution with CO₂. After loading, a device to measure the volume of gas evolved was sealed onto the cell and the quinone was oxidized electrochemically to release CO₂. In a 0.05M di-t-butyl benzoquinone in the RTIL about 0.03 mol CO₂/L solution was pumped from 0.085 atm to 0.30 atm as determined by gas chromatography. Under the experimental conditions, about 2.6 times the theoretical minimum energy was required to pump CO₂, far better than that of other techniques.

Oral Presentation
**From one greenhouse gas to another:
the biological conversion of CO₂ to methane**

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Biological methane formation is a microbial process unique to methanogens, which are Archaea, the third kingdom of life. This process occurs in most oxygen-depleted environments, such as the digestive tract of many animals including humans; in ruminants, it occurs in the rumen. Methanogens produce ~10⁹ tons of methane annually. Understanding the mechanism of methane formation is critical because methane is an important fuel and a potent greenhouse gas whose concentration is rising at a rate of 1% per year. Thus, methane is a major contributor to global warming. We are determining the mechanisms of three key enzymes involved in methanogenesis from acetic acid. These enzymes are CO dehydrogenase/acetyl-CoA synthase (CODH/ACS), methyl-CoM reductase (MCR), and heterodisulfide reductase (HDR). We have used a battery of spectroscopic and kinetic approaches to understand the remarkable mechanisms of these proteins. In the bifunctional nickel iron-sulfur protein CODH/ACS, we have found that the CODH and ACS active sites communicate to coordinate carbon flow and electron transfer. Our studies on the Ni-tetrapyrrole containing MCR indicate strict requirements for oxidation state (Ni(I)) and coordination state (five-coordinate) for activity. Our results also indicate that the cofactor, Coenzyme B, is integrally involved in the steps leading up to methane formation. Our studies also are consistent with the involvement of several unusual radical based intermediates in the MCR-catalyzed reaction. The studies are leading to important insights into how natural gas is formed in nature and into the structure and function of metals in biology.

In a multidisciplinary project, we have been targeting enzymes involved in methanogenesis to tackle the problem of global warming. Our results indicate that this is a feasible strategy to inhibit methanogenesis in ruminant organisms.

This work has been supported by DOE Grant ER20297 and an ARD Grant from the University of Nebraska.

Oral Presentation

Amorphous Vanadium Phosphate Catalysts from Supercritical Antisolvent Precipitation

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Crystalline vanadium phosphate catalysts (VPO)^{1,2} are the only example of a commercial heterogeneous partial oxidation catalyst for the activation of alkanes. Since their discovery in 1968, these catalysts have been the focus of intense research to improve their activity, which is generally accepted as being associated with the crystallinity of the catalysts. Indeed, over a thousand papers and patents have addressed this complex catalyst system, but mainly focusing on the preparation and testing of crystalline catalysts. Recently, we have shown that three materials prepared by three conventional methods, designated as VPA, VPO and VPD respectively, give final catalysts that have similar activity per unit surface area of catalyst even though the catalysts comprise differing relative amounts of crystalline (VO)₂P₂O₇ and VOPO₄ polymorphs³. The identical catalytic performance could, in principle, be ascribed to a common overlayer that is stabilised on the crystalline subsurface (whether it be (VO)₂P₂O₇ or VOPO₄) by the reaction conditions (i.e. partial pressures of butane and oxygen, and, temperature). Indeed detailed TEM studies of the catalysts has indicated that an amorphous layer 1- 2.5 nm in thickness exists on the surface of the crystalline (VO)₂P₂O₇ phase⁴ although the origin of this overlayer is uncertain and its role in catalysis is controversial. Here we describe a new preparative route to VPO using antisolvent precipitation with supercritical CO₂ to generate microspheroidal VPO, designated VPO_{sc}, which is entirely amorphous yet produces a catalyst with an activity per unit area comparable to crystalline VPO catalysts prepared conventionally. VPO_{sc} was evaluated as a catalyst for the partial oxidation of butane to maleic anhydride in a standard laboratory microreactor. From these results it is clear that the new vanadium phosphate catalyst (VPO_{sc}) prepared using supercritical precipitation offers two distinct advantages over previous catalyst preparation methods. First, and most interestingly, VPO_{sc} does not require an extensive pretreatment time in the reactor. Stable catalytic performance is attained (and maintained for over 100 h) as soon as the catalyst reaches the required operating temperature. In contrast, the catalysts based on the industry standard precursor, VOHPO₄·0.5H₂O, always require 24-72h in the microreactor to achieve stable catalytic performance⁵. Second, the new VPO_{sc} is apparently more active for maleic anhydride production than the standard vanadium phosphate catalysts. This finding throws doubt on the currently accepted view for the origin of the activity of VPO catalysts and the role of crystalline phases. Our material, activated at 400° C for 50h seems to comprise of a stable bulk amorphous VPO active phase which removes all doubts about the activity of amorphous materials. Our results give the first clear and definitive demonstration that a non-crystalline vanadium phosphate catalyst may be the preferred material for the selective oxidation of butane to maleic anhydride. Given the flexibility of the supercritical preparation method, i.e. the range of organic solvents that can be used together with the various experimental CO₂ parameters for this preparation methodology, we consider that VPO_{sc} could represent a new future for commercial amorphous vanadium phosphate catalysts; a field previously dominated by highly crystalline materials derived from crystalline VOHPO₄·0.5H₂O. Our studies show that the crystalline material, that has been the object of study for over 30 years, may only be an elegant support for an amorphous active surface layer.

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Oral Presentation

CO₂ HYDROGENATION TO LIQUID HYDROCARBON FUELS

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CO₂ hydrogenation to high quality liquid fuels, e.g. sulfur- and aromatics-free diesel, can be seen as one potential way for chemical utilization of CO₂. In a future situation where hydrogen may be available from nonfossil sources in large quantities, a liquid hydrocarbon transportation fuel fits into present day distribution infrastructures and vehicle engine technologies. Earlier studies already indicated the possibility of CO₂ hydrogenation under Fischer-Tropsch reaction conditions in principle (Weatherbee 1984). Subsequent studies concentrated mainly on catalyst screening (Choi 1996), only very limited attention was paid to the understanding of the reaction itself, e.g. mechanism and kinetics.

Here, results of a kinetic study will be presented. The main reaction path was found to be first the formation of CO via the CO₂ shift reaction followed by the subsequent hydrogenation of CO in the Fischer-Tropsch reaction. However, in agreement with Fiato (1998), also a direct hydrogenation of CO₂ can not be excluded. Assuming for the kinetic analysis a reaction scheme, consisting of these three reactions, a good correlation of the experimental data with calculated conversions and yields could be achieved. A further evidence, that CO acts as an intermediate product, was obtained by a comparison of the transient initial catalyst behavior using a H₂/CO and a H₂/CO₂ feed gas. Time pattern of catalyst activity and selectivity development were almost identical in both cases, only the duration of the individual episodes was much longer with CO₂ caused by the lower CO partial pressure (Schulz 1999). Additionally performed catalyst characterization studies, e.g. by mössbauer spectroscopy, using the H₂/CO₂ feed gas indicated that the development of the individual episodes is accompanied by changes of catalyst phase composition, mainly iron carbide is formed on the expense of iron metal and oxide.

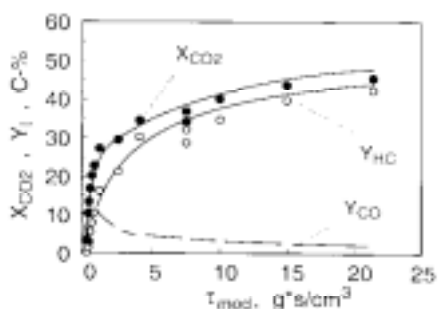


Figure 1: CO₂ conversion, CO and HC yield as function of modified residence time; fixed bed micro reactor, 300 °C, 1 MPa, (H₂/CO₂)_{in}=3/1 mol/mol; catalyst: Fe/Cu/K/Al.

The experimental results exhibit that limitation of single pass conversion exists. Thermodynamic calculations indicate that this is mainly attributable to equilibrium constraints due to the large amounts of H₂O produced. H₂O is also known to have a negative effect on chemical reaction kinetics. Therefore, future activities in the present investigation will focus on reactor configurations, allowing for in-situ removal of H₂O, e.g. by membranes. This may also be of interest for the Fischer-Tropsch synthesis on Fe-based catalysts with synthesis gases both from natural gas and biomass.

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Oral Presentation

The CO₂ Reforming of Methane and Related Reactions

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There has been considerable interest over the last few years in the development of catalysts for the production of syngas with low H₂/CO ratios by either partial oxidation:



or CO₂ ('Dry') reforming:



The main problem in developing catalysts for the dry reforming and related reactions is that carbon deposition becomes significant with almost all materials. Although it has been claimed that special catalyst formulations allow Ni-containing materials to be used, most such catalysts succumb to very substantial levels of carbon deposition under more extreme operating conditions or after longer times of operation [1]. Noble metal formulations have also been examined for the reaction and several of these such as Pt/ZrO₂ [2,3] show some promise.

Another approach to obtaining stable dry reforming catalysts which has recently been described in the literature is the use of metal carbides. York et al. [4,5,6] have shown that it is possible to use binary and ternary carbides of the Group V and VI metals for dry reforming but that only those carbides of molybdenum and tungsten were active and stable, these displaying activities comparable to supported metal catalysts without giving evidence of any carbon deposition. Yorke et al. also reported that these materials were active for steam reforming or for reforming with air (partial oxidation). The same authors have recently published thermodynamic data showing that the carbides have a stability in the order Mo₂C, WC > VC_x > NbC_x > TaC_x and that this order accords with the order of catalytic stabilities which they had determined [6].

This contribution will discuss some of the potential uses of CO₂ reforming and the thermodynamics of the reaction, showing that use of the reaction will not contribute to a reduction of CO₂ emissions as suggested by many authors. Having reviewed some of the catalyst systems described in the literature for CO₂ reforming, it will then cover some aspects of the development and testing of Pt/ZrO₂ catalysts for this reaction and will also give some recent results obtained relating to the stabilities of the carbides of tungsten and molybdenum described above which show that these materials are only stable under very well defined conditions.

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Oral Presentation

The onset of life and the dawn of oxygenic photosynthesis: Respective roles of $[\text{Fe}_4\text{S}_4]^{2+}$ cubane and transient $[\text{Mn}_4\text{O}_4]^{6+}$ in CO_2 reduction

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4.4 billion years ago the Earth was a giant photoelectrochemical cell with a potential of more than half a volt, commensurate with the needs of chemosynthetic life. The cool carbonic acid ocean was the fluid matrix to a dispersed positive electrode, $\gamma\text{-Fe}^{\text{III}}\text{OOH}$, generated by UVC on $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ supplied, along with Mn^{2+} , through 400°C submarine springs ($2\text{Fe}^{2+} + 2\text{H}^+ + h\nu \longrightarrow 2\text{Fe}^{\text{III}} + \text{H}_2$). The H_2 was lost to space. Yet a hydrogen electrode was maintained at cooler, deep, alkaline springs through the reduction of water as ferrous silicates and residual meteoritic nickeliferous iron were oxidized during hydrothermal convection within the crust (e.g. $3\text{Fe} + 4\text{H}_2\text{O} \longrightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2$). Titration of this H_2 -bearing hydrothermal fluid (containing simple organic molecules generated in the same milieu) with the acid ocean was inhibited by the precipitation of membranous barriers of $\text{FeS} \gg \text{FeNi}_2\text{S}_4$ and $\sim\text{Fe}^{\text{II}}_2\text{Fe}^{\text{III}}(\text{OH})_7$. These films prevented direct neutralization while permitting restricted e^- and small molecule flow as well as the operation of a natural protonmotive force to drive PPI production from Pi. The electrons were drawn through the FeS conductor that comprised the barrier, to the $\gamma\text{-Fe}^{\text{III}}\text{OOH}$, the electron terminal, which had been eddy-pumped to the ocean floor. Thus H_2 was adsorbed and activated on the inner surface by FeS to react with CO (later with CO_2). Products were prepared for phosphorylation, interaction and polymerization. Therefore these inorganic bubbles, constantly supplied with fuel as well as small reduced organic molecules, CO, CO_2 , phosphate and trace metals, constituted the combinatorial chemical reactor from which chemosynthetic life emerged.

Genetic control was rudimentary in these early metabolists, so only self-assembling clusters could be relied upon as co-opted catalysts and electron transfer agents. Chief amongst these were the 'ready made' $[\text{Fe}_4\text{S}_4]^{2+}$ cubanes which either contributed to the mineral greigite (as $[\text{Fe}_4\text{S}_4][\text{SFeS}]_2$), or, in the presence of newly generated amino acids, to the active thiocubane in the electron-transfer agent, ferredoxin ($[\text{Fe}_4\text{S}_4][\text{SR}]_4^{2-/3-}$) (Russell et al. 1994, J. Mol. Evol. 39, 231). Also the comparable mineral violarite (as $[\text{Fe}_2\text{Ni}_2\text{S}_4][\text{SNiS}]_2$) could have acted as a primitive CO- dehydrogenase. Certainly it is structurally similar to the active center of this enzyme ($[\text{Fe}_4\text{S}_4][\text{SR}]_4\text{Ni}$) (Ragsdale & Kumar 1996, Chem. Rev. 96, 2515).

After life's emergence the next major biogeochemical revolution was the entrapment of photolytic hydrogen from water by the 'invention' of oxygenic photosynthesis. Although by this time the genetic system was well developed, we might expect that such an evolutionary jump requires that the metal complex permitting the transfer of 4 electrons, initially from HCO_3^- , to O_2 waste, $[\text{CaMn}_4\text{O}_x(\text{HCO}_3)_y]$ (Dismukes et al. 2001, PNAS 98, 2170), be also self-assembling. By this time ($\sim 4\text{Ga}$) the ocean was neutralized and a natural *pmf* no longer operated. Hot springs near the surface would have still disgorged Fe and Mn to the ocean. We suggest that Fe, being less soluble at higher pH, would have largely precipitated around the spring, leaving $[\text{Mn}^{\text{II}}_2(\text{HCO}_3)_4]_n$ (Dismukes et al. *ibid.*) to be photo-oxidized ($\lambda \sim 225\text{nm}$; cf. Anbar & Holland 1992, GCA 56, 2595), in the presence of Ca, to colloidal clusters of $[\text{CaMn}_4\text{O}_9 \sim 3\text{H}_2\text{O}]$ perhaps with the reduction of Fe^{III} . The composition of the cluster is comparable with the O_2 -evolving polymorphic complex (where Ca could stabilize a hypothetical transient $[\text{Mn}_4\text{O}_4]^{6+}$ cubane core prior to the formation and release of O_2) within photosystem II that 'captures' the reducing power of H_2 , *via* NADPH, to fix CO_2 (see Dismukes et al. 1998, in Garob, G. ed. Proc. XI Int. Photosynthesis Cong., v. II, Kluwer Academic Publishers, 1259) (and cf. hausmannite as $[\text{Mn}_4\text{O}_4][\text{OMnO}]_2$). Protons released from the water-oxidizing complex at the same time contribute to a 'manufactured' *pmf* which drives ATP synthesis. In the absence of a chelating agent the putative cubane would be destined to reconform to comprise the mineral ranciéite ($\text{CaMn}_4\text{O}_9 \sim 3\text{H}_2\text{O}$, Kim 1993 N. Jb. Miner. Mh. 233).

Poster Presentation
CATALYTIC DEHYDROGENATION OF HYDROCARBONS
IN THE PRESENCE OF CARBON DIOXIDE

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Introduction

The authors reported the effects of CO₂ on the catalytic dehydrogenation of hydrocarbons such as ethylbenzene, and propane [1-3]. In the present conference, the results obtained in the further study are presented.

Dehydrogenation of ethylbenzene over a Fe₂O₃/Al₂O₃ catalyst

The effects of reaction conditions on the yield of styrene in the dehydrogenation of ethylbenzene over a Fe₂O₃/Al₂O₃ in the presence of CO₂ and in the presence of He as an inert gas were investigated at 798-848 K under atmospheric pressure. The yield of styrene increased with an increase in W/F in the reaction both in the presence of CO₂ and He, where W and F are the weight of the catalyst and the flow rate of ethylbenzene, respectively, and reached its highest value around at 40 g-cat/min/mmol-EB in W/F. The highest yield of styrene in the dehydrogenation in the presence of CO₂ was higher than that in the dehydrogenation in the presence of He, and also higher than that at the equilibrium of the dehydrogenation in the presence of He, probably because CO₂ reacted with H₂ produced by the dehydrogenation. The yield of styrene increased with increasing reaction temperature, but the selectivity to styrene decreased and the amount of carbon deposited on the catalyst during the reaction increased. The decrease in the catalyst activity with time-on-stream was much smaller during the dehydrogenation in the presence of CO₂ than during the dehydrogenation in the presence of He.

Dehydrogenation of lower alkanes over a Cr₂O₃/SiO₂ catalyst and a Ga₂O₃/SiO₂ catalyst

The catalytic performances of a Cr₂O₃/SiO₂ catalyst and a Ga₂O₃/SiO₂ catalyst for the dehydrogenation of lower alkanes such as propane, ethane, butanes in the presence of CO₂ and Ar were compared at 823 K under atmospheric pressure. The dehydrogenation activity of the Cr₂O₃/SiO₂ catalyst was much higher than that of the Ga₂O₃/SiO₂ catalyst. However, the decrease in the activity of the Cr₂O₃/SiO₂ catalyst during the dehydrogenation was much larger than that in the activity of the Ga₂O₃/SiO₂ catalyst, and the coke deposition over the Cr₂O₃/SiO₂ catalyst was also much higher than that over the Ga₂O₃/SiO₂ catalyst. The yields of alkenes in the dehydrogenation over the Cr₂O₃/SiO₂ catalyst in the presence of CO₂ were 10-40% higher than those in the absence of CO₂, whereas those in the dehydrogenation over the Ga₂O₃/SiO₂ catalyst in the presence of CO₂ were 10-30% lower than those in the absence of CO₂. Isobutane was the most reactive in the dehydrogenation over both catalysts, and ethane was the least reactive.

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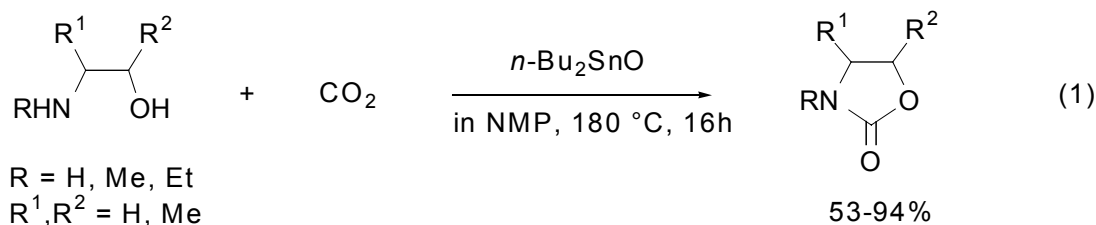
Oral Presentation

Synthesis of 2-Oxazolidinones from CO₂ and 1,2-aminoalcohols Catalyzed by *n*-Bu₂SnO

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The dehydrative condensation of 1,2-aminoalcohols with CO₂ is one of the most convenient methods for the synthesis of 2-oxazolidinones, which are useful synthetic intermediates for pharmaceutical, agricultural, and other chemicals. The dehydrating agent such as phosphorus compounds¹ or carbodiimides² is usually used in order to eliminate the water formed during the reaction. On the other hand, the reaction of 1,2-alkylaminoalcohols with CO₂ has been known to proceed without any dehydrator to give 3-alkyl-2-oxazolidinones in the presence of triphenylstibineoxide (Ph₃SbO) as catalyst³ or even without any catalyst.⁴ However, these reaction systems failed to promote the corresponding reactions with 1,2-aminoalcohols without substituent on their nitrogen atom such as ethanolamine.³

We report that commercially available dibutyltin oxide (*n*-Bu₂SnO) can catalyze the reaction of various 1,2-aminoalcohols with CO₂ to give 2-oxazolidinones in fair to excellent yields (eq. 1). The effect of the amount of catalyst and that of solvent will be discussed.



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Oral Presentation
**Electrochemical Activation of Carbon Dioxide to Carbon Monoxide or Acetate
by Enzymes in *Clostridium thermoaceticum***

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Carbon Monoxide Dehydrogenase (CODH) from *Clostridium thermoaceticum* is Ni and Fe containing metalloenzyme which catalyzes two types of reactions: the reversible oxidation of CO to CO₂ and the synthesis of acetyl coenzyme A which is a precursor of acetic acid *in vivo*. We applied both activities of CODH to the electrochemical activation of CO₂ to CO or acetic acid using CODH and other components in *Clostridium thermoaceticum*. First, in the presence of CODH, carbon dioxide reduction occurred when the potential was lowered below - 550 mV vs. NHE (pH = 6.3, 0.1 M phosphate buffer, CO₂ saturated) with a mediator. CO was the sole product with about 100 % current efficiency when the solution was electrolyzed at - 570 mV. The overvoltage of CO₂ reduction to CO by CODH is only ~ 100 mV. The turnover number was measured to be 700 h⁻¹ and the pH optimum was about 6.3 where the enzyme stability and proton assisted reduction compromise each other. Second, if CODH and other protein components in *Clostridium thermoaceticum* were used together, selective carbon dioxide reduction to acetate could be achieved with more than 90 % current efficiency. This is an apparent 8 electron reduction of CO₂ and *in vitro* acetate production without coenzyme A was successfully accomplished.

Oral Presentation

Adsorption and reaction of CO₂ on Mo₂C catalyst

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In searching new and effective catalysts, Mo₂C is obviously unique in many respects. One of its most interesting properties is that its combination with ZSM-5 effectively catalyzes the direct conversion of methane into benzene (1,2). Supported Mo₂C is also an active catalyst for the hydrogenation of CO₂ into hydrocarbons (3), and for the CH₄+CO₂ reaction to give synthesis gas (4). Recently we found that it effectively catalyses the oxidative dehydrogenation of ethane and propane using CO₂ as an oxidant. The presence of alkali additives appreciably enhanced the catalytic activity of Mo₂C in most of these reactions. In our paper we deal with the following subjects: (i) interaction of CO₂ with Mo₂C prepared on Mo(100) surface with several tools of surface science in UHV, (ii) the reaction of CO₂ with Mo₂C at high temperature, (iii) effects of potassium on the above processes, and (iv) reaction of CO₂ with various hydrocarbons.

Methods used are: high resolution electron energy loss spectroscopy (HREELS), X-ray photoelectron spectroscopy (XPS), Fourier transform IR spectroscopy (FTIR) and thermal desorption spectroscopy (TPD). Supported Mo₂C catalyst was prepared by the carburization of calcined MoO₃/SiO₂ in CH₄+H₂ gas mixture. Catalytic reaction was carried out at 1 atm of pressure in a fixed-bed, continuous flow reactor consisting of a quartz tube connected to a capillary tube. Reaction products were analyzed by gas chromatograph.

CO₂ adsorbs mostly weakly and reversibly on Mo₂C/Mo(100) surface. However, the appearance of a small CO peak (Tp=360 K) following CO₂ adsorption suggests that a fraction of CO₂ underwent dissociation on the active sites of Mo₂C. Potassium adlayer dramatically affects the adsorption and reactivity of CO₂ on Mo₂C and it leads to the formation of negatively charged CO₂. This species dissociates even at 120 K. CO formed further decomposes to C and O. Their recombinative desorption occurs in several high temperature peaks between 850- 1100 K. Using labeled CO₂, ¹³CO₂, we obtained that 50-60% of CO released come from the oxidation of the carbon of Mo₂C with the CO₂.

The decomposition of gaseous CO₂ to CO on highly dispersed Mo₂C deposited on SiO₂ proceeds under isotherm conditions with a measurable rate above 873 K. As revealed by XPS we can count with the simultaneous formation of Mo²⁺, Mo⁴⁺ and Mo⁶⁺ as result of the oxidation of Mo₂C. Complete oxidation to MoO₃ can not be achieved up to 1023 K.

In the study of the oxidative dehydrogenation of ethane with CO₂ on Mo₂C/SiO₂ at 850-923 K we found that ethylene is produced with 90-95% selectivity at a conversion of 8-30% . In the case of propane, the selectivity of propylene was 85-90% at 943 K. It is assumed that Mo oxycarbide formed in the reaction between CO₂ and Mo₂C plays an important role in the activation of hydrocarbons.

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Oral Presentation

Rubisco: How to Make a Better CO₂-Fixing Enzyme

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Ribulose-1,5-bisphosphate carboxylase/oxygenase (Rubisco) catalyzes the rate-limiting step of photosynthesis. It captures atmospheric CO₂ by carboxylating ribulose 1,5-bisphosphate (RuBP) and producing two molecules of 3-phosphoglycerate, thereby serving as the primary point of entry of carbon into all life on the planet. Although Rubisco may be the most abundant protein in nature, it may also be the slowest with a carboxylation k_{cat} of only several per sec. O₂ competes with CO₂ at the active site, further reducing net CO₂ fixation. Oxygenation of RuBP generates 3-phosphoglycerate and phosphoglycolate, and this latter, nonessential metabolite leads to the loss of CO₂ during conversion of glycine to serine in the photorespiratory pathway. Thus, there has been much interest in engineering Rubisco to increase its CO₂/O₂ specificity (Ω) by increasing the k_{cat}/K_m of carboxylation (V_c/K_c) relative to that of oxygenation (V_o/K_o). However, an increase in Ω ($V_c K_o/V_o K_c$) is not beneficial if it leads to a substantial decrease in V_c (and a decrease in net CO₂ fixation). Rubisco is also one of the largest enzymes on earth being comprised of eight, 55-kD large subunits and eight, 16-kD small subunits. X-ray crystal structures have revealed that the active site is formed by residues from the C-terminal, α/β -barrel domain of one large subunit and residues from the N-terminal domain of a neighboring large subunit. The precise role of the small subunit in Rubisco structure and function is not known. It has been difficult to apply genetic methods for manipulating the Rubisco of prokaryotes and plants. In most eukaryotes, the large subunit is coded by the polyploid chloroplast genome, and the small subunit is coded by a family of genes in the nucleus. Only in the green alga *Chlamydomonas reinhardtii* has it been possible to reduce or eliminate all of these gene copies so that both genetic screening/selection and nuclear/chloroplast transformation can be used to assess the structure-function relationships of the enzyme. Taking advantage of the fact that *Chlamydomonas* can survive in the absence of photosynthesis when supplied with acetate, genetic screening and selection identified several large-subunit regions far from the active site in which amino-acid substitutions decreased Ω and second-site suppressors increased it back to the wild-type value. When directed mutagenesis and chloroplast transformation were used to change the identities of residues in these regions to those characteristic of the higher- Ω plant enzymes, Ω was, in fact, decreased. This indicates that there must be other residues that can complement such deficiencies and contribute to catalytic efficiency. With regard to the small subunit, suppressor substitutions in a loop between two β strands have been found to compensate for the decreases in Ω , V_c , and thermal stability that arise from a substitution in the large subunit. This small-subunit loop is 20 Å away from the active site, but directed mutagenesis has shown that a single substitution in the loop can decrease Ω and V_c . In conclusion, the prospects for producing a better Rubisco improve as we gain a deeper understanding of the enzyme's structure-function relationships. This research is supported by grants from the USDA and DOE.

Poster Presentation

Ring-Opening Polymerization of Cyclic (Di)esters in Supercritical Carbon Dioxide

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Dissemination of volatile organic compounds in the environment is nowadays one of the most worrying environmental concerns, which explains the search for more environmentally friendly production conditions. One promising technique relies upon the use of supercritical carbon dioxide as a sustainable alternative to organic solvents. Production of polymeric materials in supercritical carbon dioxide has been reported over the last ten years.^{1,2} Aliphatic polyesters, such as poly(ϵ -caprolactone) (PCL), polylactide (PLA) and polyglycolide (PGA), are of great interest for biomedical applications, due to biodegradability and biocompatibility. Such polymers are easily prepared by coordination-insertion ring-opening polymerization of the parent monomers.

We have recently reported on the successful ring-opening polymerization (ROP) of cyclic (di)esters (ϵ -caprolactone, lactide) using dibutyltin dimethoxide as an initiator. The kinetics of the precipitation ROP of ϵ -caprolactone in sc CO₂ (40 °C, 210-215 bar) has been studied and the reaction proved to be controlled.³ ROP of (L,L)-lactide has also been conducted in sc CO₂.

The precipitation polymerization can be changed into a dispersion polymerization when a stabilizer is added to the polymerization medium. For example, microspheres of poly(ϵ -caprolactone) (PCL) are formed in the presence of a diblock copolymer of poly(ϵ -caprolactone) and poly(1H,1H,2H,2H-perfluorodecyl acrylate).

Having determined the phase diagram of mixtures of ϵ -caprolactone and CO₂, we are now paying attention to the extraction of the residual monomer by SCFE (supercritical fluid extraction) in order to recover high purity polymers required when biomedical applications are envisioned.

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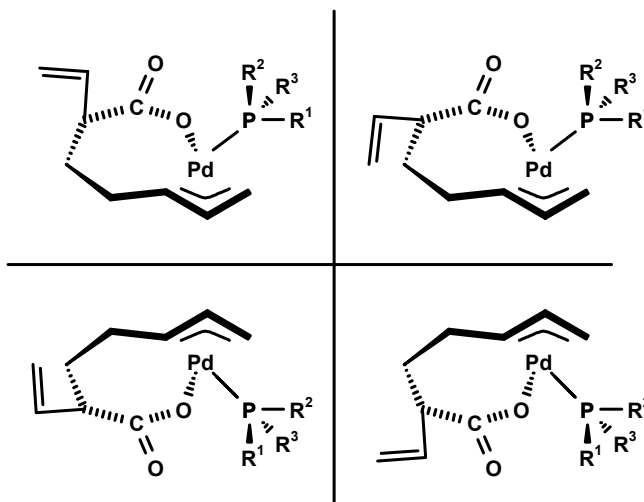
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Poster Presentation
Stereochemical Control of Coupling Butadiene and CO₂ at Palladium Centres.

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The palladium-catalyzed coupling between butadiene and carbon dioxide occurs under formation of the racemic δ -lactone (E)-2-ethylidene-hept-6-ene-5-olide.¹ The catalytic cycle of the reaction has been discussed in the literature extensively.² Consecutive reactions of enantiopure δ -lactone would open an access to interesting products. Efforts to establish an enantioselective catalytic synthesis of δ -lactone by use of chiral co-ligands remained however unsuccessful.³



In order to understand the stereochemistry of the reaction in more detail an investigation focusing on the key intermediates of the catalytic cycle was necessary. Here, we report on stoichiometric syntheses of diastereomeric octadienediylpalladium complexes containing chiral phosphine ligands and their stereochemical transformations in the CO₂ insertion step. These results reveal that a stereochemical control of certain key steps should be possible and could open an access to enantiopure coupling products.

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Poster Presentation
**POTENTIAL CLEAN DEVELOPMENT MECHANISM PROGRAM IN
PERTAMINA – INDONESIA**
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The conference of parties-COP is the “supreme body” of the Climate Change Convention held its first session in Berlin from 28 March – 7 April, 1998. The convention required COP-1 to review whether to commitments of developed countries to take measures aimed at returning their emission to 1990 levels by the year 2000 were adequate for meeting the convention's objective.

The second session of the COP was held from 8 – July 1 1996 in Geneva. The third session took place in Kyoto, Japan from 1 – 12 December 1997 and adopted the Kyoto Protocol.

Indonesia as an non Annex-1 country has not been ratified Kyoto Protocol and still waiting for the developed countries (Annex-1) ratified it. If the developed countries ratified Kyoto Protocol, a Clean development Mechanism (COM) will grant country credits for financing developing countries (non Annex-1) projects which have aimed to avoid emissions and promoting sustainable development.

A Joint Implementation (JI) programme will offer credits for contributing to projects in other developed countries and international emission trading regime will allow developed countries to by and shell emissions credit among themselves

In Indonesia, carbon dioxide (CO₂) emission from fossil fuels-use predicted, will increase from 154 million ton by the year 1991 to 1139 million to by the year 2021, or increase about 6,9 % a year. PERTAMINA as an oil and gas industries in Indonesia have a chance to reduce carbon dioxide emission to returning greenhouse gases emission.

This paper studied several aspect related of Clean Development Mechanism program in PERTAMINA operation to reduce greenhouse gases emission such geothermal energy, unleaded gasoline, etc.

Oral Presentation

Metal-Carbon Bond Characters of Reaction Intermediates in Multi-electron Reduction of CO₂ Catalyzed by Ruthenium Complexes

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Multi-electron reduction of CO₂ is energetically favored compared with one- and two-electron reduction of CO₂, since the equilibrium potential shifts progressively to a positive direction as the number of electrons participated in the reduction increases. If multi-electron reduction of CO₂ on metal complexes is assumed to proceed according to eq. 1, reductive metal-carbon bond cleavages of these species would produce HCOOH, CO, H₂CO, CH₃OH and CH₄ in protic media as the two-, four-, six- and eight-electron reduction products. Free energy changes of multi-electron reduction of CO₂, therefore, may be correlated with the strength of the M-C(O)OH, M-CO, M-CHO, M-CH₂OH, and M-CH₃



bonds. Along this line, a series of [Ru(bpy)₂(CO)L]ⁿ⁺ (L = CO₂, C(O)OH, CO, CHO, CH₂OH, CH₃ and CH₃C(O); n = 0, 1, 2) were prepared (Fig. 1) to compare the bond characters from the Ru-CO₂ bond to the Ru-CH₃ one based on the Ru-L bond length and the ν(Ru-L) band.

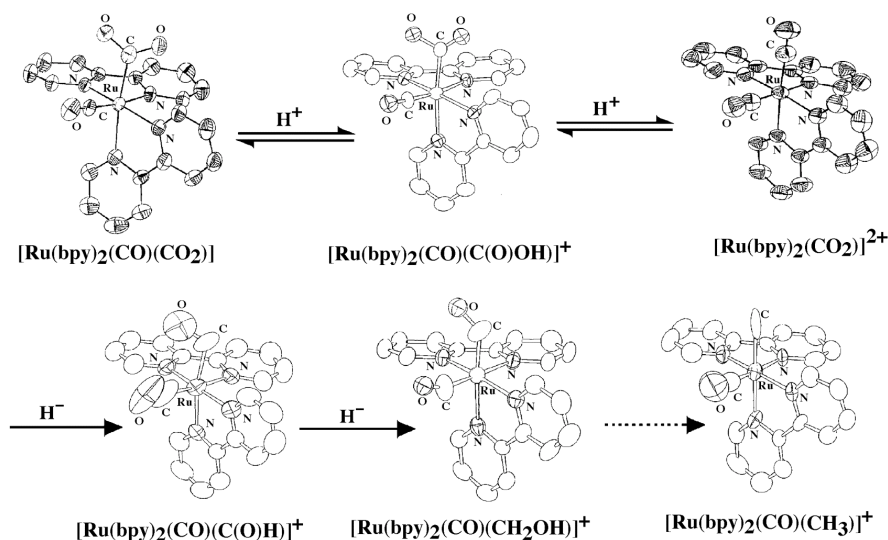


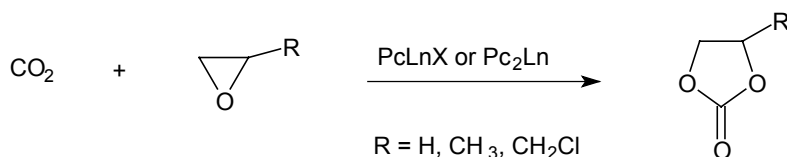
Figure 1. Crystal Structures of a series of [Ru(bpy)₂(CO)L]ⁿ⁺ (L = CO₂, C(O)OH, CO, CHO, CH₂OH, CH₃ and CH₃C(O); n = 0, 1, 2)

Oral Presentation
**APPLICATIONS OF PHTHALOCYANINE COMPLEXES FOR CARBON DIOXIDE
FIXATION**

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The increasing of the CO₂ concentration in the atmosphere is now a global environmental issue. As a solution for this serious problem, the reduction of carbon dioxide is studied by many workers to convert it into useful materials. We proposed that one of the most perspective way which give possibility to remove carbon dioxide from atmosphere on a long time is transformation it into ecologically safe polymers (for example polypropylene carbonate). The catalytic reaction of carbon dioxide with olefine oxides was investigated by chemical and electrochemical methods. For the first time substituted phthalo- and diphtalocyanine complexes of rare earth elements as catalysts were used¹. The high solubility of the most compounds obtained provide the reaction proceeding in the conditions of homogenous catalysis on the scheme:



The structure of the compounds obtained and their individuality were confirmed by IR and NMR ¹H and ¹³C spectra.

Suitable methods for synthesis of substituted diphtalocyanines of the different elements have been developed². This diphtalocyanines have been synthesized practically for all elements of the rare earth series. By changing the substituents in present molecules we synthesize new materials which can be used for the reduction of carbon dioxide into useful materials such as C₂H₄, CO, HCOOH and CH₃OH.

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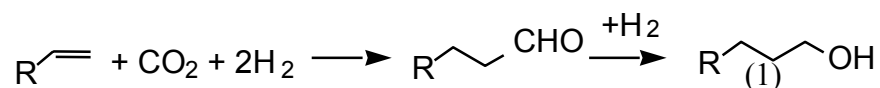
The authors thank the Russian Foundation for Basic Research for financial support (No 00-03-32658).

Oral Presentation
Hydroformylation using carbon dioxide as a reactant

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In contrast to carbon dioxide (CO₂), carbon monoxide (CO) is much more reactive and is used as a reactant in many processes. Among them, hydroformylation is the oldest and largest one catalyzed by transition metal complexes; it produces more than six million tons of chemicals per year worldwide. On the other hand, as a C₁ molecule, CO₂ has such advantages as to be non-toxic and abundant. Recently, we could find a new hydroformylation in which CO₂ is directly used as a reactant (eq. 1) [1].



The tetranuclear ruthenium complexes such as H₄Ru₄(CO)₁₂ are the effective catalysts for this reaction. When cyclohexene is used as a substrate, the yield of the corresponding alcohol reaches about 90 %. A key step of this reaction is the hydrogenation of CO₂ to CO catalyzed by the tetranuclear ruthenium complexes [2].

One of the undesirable side-reaction is a simple hydrogenation of alkene, which occurs at the initial stage of this reaction. We have investigated the time dependency of the ruthenium complexes by IR spectroscopic analysis. At the initial stage, only the tetranuclear complexes are observed, while they are partly transformed into trinuclear one as the reaction proceeds. This appears to mean that the former are not only the active species for the hydrogenation of CO₂ to CO, but also those for the hydrogenation of alkene, and that the latter is the active species for hydroformylation. The details of this reaction will be described in the conference.

This study was supported by Industrial Technology Research Grant Program in '00 from the New Energy and Industrial Technology Development Organization (NEDO) of Japan.

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Oral Presentation
**Dense Phase Carbon Dioxide as a Reaction Medium
for Homogeneous and Biphasic Catalysis**

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Dense phase (liquid or supercritical) carbon dioxide as an alternative reaction medium offers the potential for improvements in catalytic processes with respect to environmental performance, reactivity and selectivity as well as product recovery and catalyst recycle. Dense phase carbon dioxide is an effective environmentally benign solvent for a wide range of homogeneous catalytic transformations including: hydroboration; asymmetric hydrogenation and hydrogen transfer; selective oxidation of olefinic substrates; palladium-catalyzed carbon-carbon bond forming reactions; and reactions that utilize carbon dioxide as both a reagent and a solvent. Partially fluorinated ligands have been developed which impart increased solubility and catalytic performance to late transition metal complexes.

Biphasic or phase-separable catalysis combines the selectivity and catalyst/ligand design advantages of homogeneous catalysis with the product recovery and catalyst recycle advantages of heterogeneous catalysis. In biphasic catalysis, reactants and products are dissolved in a liquid phase and transition metal catalysts are immobilized in another phase, either liquid or solid. We have developed several biphasic catalysis concepts that incorporate dense phase carbon dioxide as one phase along with an immiscible solvent such as water or a room temperature ionic liquid or a polymeric support. The use of carbon dioxide allows for unprecedented control of phase behavior, solubility (of catalysts, ligands and polymeric supports), and mass transfer through simple changes in reaction conditions (i.e. pressure, temperature, mixing). These systems can lead to enhanced separability, reactivity and in some cases, selectivity relative to conventional organic solvents.

Poster Presentation
Comparison of Carbon Dioxide and Sulfur Dioxide
For Acid-Catalyzed Steam Explosion of Biomass:
a Thermodynamic Investigation.

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For the production of commodity fuels and chemicals from biomass, steam explosion pretreatment of biomass has been found to result in enhanced production of fermentable sugars when the reaction is enhanced through acid catalysis using SO₂ impregnation of the substrate. Limited reports in the literature have indicated that high temperature, high pressure CO₂, forming carbonic acid, may also offer benefits for enhanced pretreatment effectiveness in steam explosion systems. The possibility of replacing SO₂ with CO₂ offers several processing and environmental advantages and also makes use of the otherwise unused waste stream of CO₂ emanating from the fermentation processes downstream. This study compares the thermodynamic properties of these binary phase acid systems in terms of temperature and pressure influences on solubility and dissociation. Results from the analysis clarify the potential for the use of carbonic acid as a pretreatment catalyst.

Oral Presentation
**Colloid-catalyzed single-phase hydrogenation in
supercritical CO₂**

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Midway between homogeneous and heterogeneous catalysis, colloid-supported catalysts show properties and advantages from different concepts of catalysis. They are highly active, selective, and, additionally, easy to separate from other reaction components by ultra filtration. Although colloid-supported catalysts are widely used in conventional solvents, hardly anything is known about their reactivity in supercritical fluids. In contrast, especially supercritical carbon dioxide (scCO₂) has gained importance during the last decade for it is an attractive, modern alternative to conventional organic solvents. In particular, scCO₂ is non-toxic, readily available, and considered environmentally benign. Accordingly, research toward substituting traditional solvents with scCO₂ is conducted, and the first catalytic reaction is presented in which olefins and acetylenes are hydrogenated in scCO₂ mediated by a colloid-supported catalyst. The catalyst consists of bimetallic nanoparticles of catalytically active Pd surface layers atop Au cores. In a chemical reaction, the nanoparticles are formed and simultaneously deposited in block-copolymer micelles of polystyrene-*block*-poly-4-vinylpyridine. When the hydrogenations were conducted in toroid cavity autoclaves (TCA) for *in situ* NMR studies, turn-over frequencies (TOF) in the range of 10⁶ h⁻¹ were found even at the reasonably low hydrogen pressures of 15 bar. Surprisingly, the observed reactivity is much higher than it is in conventional solvents but also higher than in most other catalytic reactions. In addition, the polymeric micelles dissolve in scCO₂ without chemical modifications, e.g., without the assistance of fluorinated alkyl moieties. Optimizations of the colloid-supported catalyst and the conditions of the supercritical reaction medium are expected to yield results that even exceed the already very high TOFs measured so far. The kinetic behavior of single-phase colloid-catalyzed reactions in scCO₂ was also investigated with *in situ* NMR techniques in TCAs.

Oral Presentation
Utilization of Carbon Dioxide Using a Non-equilibrium, Microwave-induced Plasma at Atmospheric Pressure

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The utilization of CO₂ on the classical chemical way is connected with a lot of difficulties because of its high activation energy. One possibility to overcome these is the use of plasma technology to convert carbon dioxide into more valuable products.

In the last 30 years, plasma activation of CO₂ is described in many publications, but because of several technological reasons there is still no technical large scale process. The plasma activation device, built at the university of Dortmund, is planned to close this gap. It is now possible to work with streams up to 100 m³/h at atmospheric pressure using a microwave source with 6 kW.

Within the bounds of the project in Dortmund, we are looking at several reactions for CO₂ utilization, including hydrogenation, reforming reactions and hydroformylation.

Working with a non-reactive system of pure carbon dioxide, it was found that there is a maximum at 4 kW with 20 % conversion rate of CO₂ to CO and O₂. An increase of the flow rate leads to decreasing gas temperatures, because of the special properties of a non-equilibrium with nearly no additional power input. This has a positive impact on the thermodynamics of the reaction system because as higher the temperature as more CO and O₂ is reacting back to CO₂. This shows the possibility to activate even higher amounts of gas without a loss of activation efficiency.

Impressive results were obtained for the reforming reaction with methane. Conversion rates of 98 % to natural gas with a ratio of 1/1 were found for a 1/1 mixture of carbon dioxide and methane and a total flow of 80 l/min. Similar to the activation of pure CO₂, there are even higher flow rates possible to decrease the ratio of used energy to converted molecules.

The temperature of the produced natural gas will be used for further reactions on heterogeneous catalysts. The constitution of profitable products e.g. alkynes, alkenes, alcohols, aldehyds or organic acids is to be investigated.

Oral Presentation
Plasma Reduction of Carbon Dioxide with Methane

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Carbon dioxide reduction with methane has been carried out using a high-frequency pulsed plasma and a point-to-point type of reactor. A 4 kPPS (pulse per second) plasma reaction of a raw feed gas of 65% CH₄ and 35% CO₂ yields a mixture containing mainly C₂H₂ and synthesis gas of a H₂/CO ratio 2 that is suitable for CH₃OH production. The amounts of H₂ and C₂H₂ are adjustable by changing the CH₄ concentration in the feed gas. Due to the high value of C₂H₂, this process has economical potential for natural gas conversion to more valuable chemicals and is contributable to the emission reduction of greenhouse gas CO₂. The influence of methane concentration and pulse frequency on product selectivity, plasma energy efficiency, production cost, and contribution to greenhouse gas reduction is evaluated.

Oral Presentation

The Use of Schiff-Base Complexes for the Catalysis of Carbon Dioxide and Epoxide Copolymerization.

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The use of well-defined homogeneous catalysts for the production of polycarbonates through the copolymerization of CO₂ and epoxides continues to receive more attention each year. This is largely due to the economic and environmental benefits of utilizing CO₂ as a C₁ feedstock.¹ These considerations are accentuated by the hazardous and expensive process currently in place industrially, which involves the interfacial polycondensation of phosgene and diols (most commonly bisphenol-A).² For some time, our group has been active in the application of carbon dioxide chemistry to the production of polycarbonates. Based on data obtained in our use of zinc salicylaldimine complexes for the copolymerization of cyclohexene oxide and CO₂,³ as well as the work of Inoue,⁴ Holmes,⁵ and Jacobsen (in the catalytic, asymmetric ring opening of epoxides),⁶ we have decided to investigate the use of the well known “N,N’-bis(salicyladene)-1,2-diaminoethane”(salen) type ligands (as well as other relevant derivatives) for this reaction.

We have synthesized Jacobsen’s catalyst (N,N’-bis(3,5-t-butylsalicyladene)-1,2-diaminocyclohexane Cr(III)Cl) and characterized it through x-ray analysis. We found it to facilitate the copolymerization of cyclohexene oxide and CO₂ producing a turnover frequency of 28.5 g polymer/g Cr/hr. Further, in the presence of N-methylimidazole the catalytic activity exhibited a significant increase producing a turnover frequency of 88.2 g polymer/g Cr/hr. (for five equivalents of imidazole). Proton NMR shows CO₂ incorporation to be > 99%. GPC analysis of the polymer gave M_n = 6783 g/mol, M_w = 9561 g/mol indicative of a narrow molecular weight distribution (PDI = 1.4). In situ IR spectral studies have been undertaken in order to elucidate the mechanistic details of this copolymerization process. The results of these studies will be discussed.

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Poster Presentation

A Novel Process for Demulsification of Water-in-Crude Oil Emulsions by Dense Carbon Dioxide

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In a novel process, CO₂ was used successfully to break water-in-crude oil emulsions. The process was tested on different types of crude oils having variable viscosities, chemistries, and asphaltene and resin contents and it proved to be versatile. Owing to the complexity and diversity of the chemical structures encountered in different types of crude oils, we studied the behavior of asphaltenic films in model oil systems having different H/C ratios (aromaticities) and resin/asphaltene ratios upon contacting them with liquid or supercritical CO₂ under a variety of thermodynamic and kinetic conditions. In general, SC CO₂ was found to perform superior emulsion resolving power compared to liquid CO₂. The putative mechanism by which CO₂ destabilizes water-in-crude oil emulsions involves asphaltene flocculation and precipitation. The emulsions break by flocculating the adsorbed asphaltenes, leading to interface desorption, film thinning, and film rupture and water coalescence. The various factors influencing asphaltene precipitation, and consequently, emulsion destabilization have been studied in model solvent systems containing asphaltenes and resins. Increasing CO₂ pressure, residence time, temperature, and degree of mixing were found to increase the rate of asphaltene precipitation. The chemical structure, elemental analysis and molecular weights of whole asphaltenes, the CO₂-soluble and CO₂-insoluble asphaltene fractions were determined. It was found that the CO₂-insoluble asphaltene fraction has the highest oxygen and nitrogen content (highest polarity), highest aromaticity (lowest H/C ratio), highest iron content, and highest molecular weight. It is apparent that CO₂ preferentially precipitates the most surface-active portion of asphaltenes leading to a substantial weakening of the viscoelastic asphaltenic film built by asphaltenes around the dispersed water droplets in the emulsion.

Poster Presentation
**The Effect of the Support Nature on the Properties of
Ru-Co-catalysts in CO₂ + C₃H₆ Reaction**

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In present work we have studied the interaction of CO₂ + C₃H₆ over Ru-Co catalysts supported on silica and alumina modified with HZSM and Na-ZSM zeolites. Recently we have studied CO₂ + C₃H₆ reaction on Ru-Co/Al₂O₃ [1]. Ru-Co systems were prepared by impregnation of a support with RuCl₃ and Co(NO₃)₂ solutions. The process was carried out in a flow system at 473-623K, 0.3-2.0 MPa, molar ratio CO₂ : C₃H₆ = 4 : 1 and V = 100 h⁻¹.

It has been found that the activity of the catalysts and composition of products depend on the support nature. The conversion of propylene over Ru-Co/SiO₂, Ru-Co/Al₂O₃ and Ru-Co/Al₂O₃ + HZSM is 17.5%, 20.5% and 36.0% respectively at 623K and 1.8 MPa. Ru-Co/Al₂O₃ + Na-ZSM is not active in the reaction. The main products of the reaction over Ru-Co/SiO₂ are C₄-alcohols (51.1%), propionic acid (25.2%), methanol (15.2%), C₃-alcohols and butyric acid. At the same conditions the basic composition of products of the reaction over Ru-Co/Al₂O₃ + H-ZSM is butyric (49.0%) and propionic (31.8%) acids, methanol (4.6%), C₄-alcohols (7.0%), formic (2.4%) and acetic (1.1%) acids. The products of the reaction over Ru-Co/Al₂O₃ contain C₁-C₄ acids and some amount of corresponding aldehydes [1]. It should be noted the traces of CO, O₂, H₂ and C₁-C₃ hydrocarbons that we detected in the products of interaction CO₂ + C₃H₆ over Ru-Co/support catalysts.

The structure and state of surface of Ru-Co/support were investigated by TEM and IR spectroscopy (CO was used as a probe molecule). These methods showed both oxidized (2165 2100 cm⁻¹) and reduced (2050-2080, 1980-1880 cm⁻¹) metal forms and formation of bimetallic Ru-Co clusters. The particles of Ru in Ru-Co/SiO₂ and Ru-Co/Al₂O₃ catalysts are of 30-40 and 40-60 respectively, these particles are uniformly distributed on the surface. The structure of Ru Co/Al₂O₃ + HZSM catalyst is not uniform and differs on different components of the support.

Thus over Al₂O₃ we observed Ru spheric particles of 50-60 consisted of small (5) particles. On zeolites an active phase is localized in cavities. The IR spectra of carbon dioxide chemisorbed on Ru-Co/support surface contain 2380-2310 cm⁻¹ (CO₂) 2030-2080 cm⁻¹ (M₂^oCO) and 1880 cm⁻¹ (M₃^oCO) adsorption bands. The intensity of 1900-1990 cm⁻¹ and 1880 cm⁻¹ (CO_{ads}) a.b. drops decreases in a sequence Ru-Co/SiO₂ > Ru-Co/Al₂O₃ > RuCo/Al₂O₃ + H-ZSM. The intensity of a.b. associated with adsorbed CO₂ grows in the same sequence. Adsorption bands assigned to M^oCO, M₂^oCO, M₃^oCO structures point to dissociative adsorption of CO₂ on Ru-Co/support catalysts that is proved by formation of alcohols and CO, O₂ in products. On zeolite containing catalysts we observed associative chemisorption of CO₂ that leads to the increase of butyric acid yield.

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